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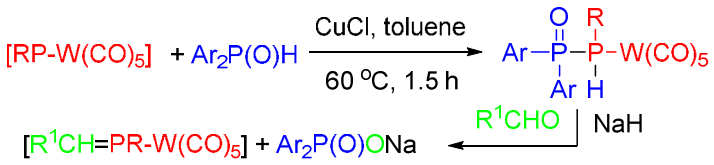
Graphical abstract



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Insertion of phosphinidene complexes into the P-H bond of secondary phosphine oxides: a new version of the phospha-Wittig synthesis of P=C double bonds

Yanwei Hao,[a] Di Wu,[a] Rongqiang Tian*,[a] Zheng Duan*,[a] François Mathey* [a,b]

Terminal phosphinidene complexes [RP-W(CO)$_5$], as generated at 60 °C in the presence of copper chloride from the appropriate 7-phosphanorbornadiene complexes, react with secondary phosphine oxides Ar$_2$P(O)H to give the insertion products into the P-H bonds. After metalation with NaH, these products react with aldehydes to give the corresponding phosphaalkenes which are trapped by dimethylbutadiene.

For a long time, the development of the carbene-like chemistry of electrophilic terminal phosphinidene complexes [RP-M] (M = Cr, Mo, W(CO)$_5$, Fe(CO)$_4$ and cationic complexes) was centered on cycloaddition reactions.[1] The systematic development of insertion reactions into A-H σ bonds is more recent.[2] Noteworthy are the insertions into Si-H[3] and B-H[4] bonds. In both cases, the reaction is favored by the interaction of the electrophilic phosphinidene phosphorus with the hydridic hydrogen. The case of P-H bond is more delicate. A secondary phosphine tend to displace the phosphinidene from its complex, thus leading to the failure of the insertion reaction. When replacing the secondary phosphine by its P-W(CO)$_5$ complex, no reaction is observed. Reactions using secondary phosphine oxides were more productive. These experiments are the subject of this report.

The copper chloride-catalyzed decomposition of 7-phospha-norbornadiene P-W(CO)$_5$ complexes **1** was used as a source of phosphinidene complexes[5]. The reaction was carried out at 60 °C in toluene or THF. Successful insertions of the phosphinidenes into the P-H bond were observed with secondary diphenyl and di-2-thienylphosphine oxides (Scheme 1).

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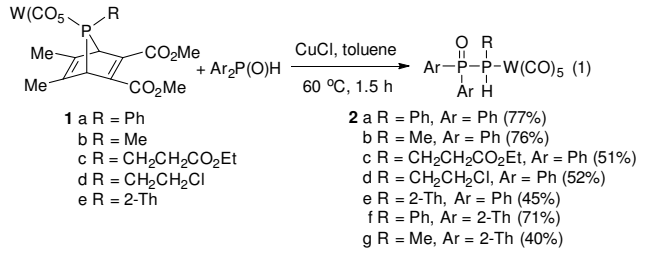
Electronic Supplementary Information (ESI) available: Synthesis and characterization of compounds **2** – **9.** X-ray data for **2a**: CCDC no 1045537



1 a R = Ph
b R = Me
c R = $CH_2CH_2CO_2Et$
d R = CH_2CH_2Cl
e R = 2-Th

2 a R = Ph, Ar = Ph (77%)
b R = Me, Ar = Ph (76%)
c R = $CH_2CH_2CO_2Et$, Ar = Ph (51%)
d R = CH_2CH_2Cl, Ar = Ph (52%)
e R = 2-Th, Ar = Ph (45%)
f R = Ph, Ar = 2-Th (71%)
g R = Me, Ar = 2-Th (40%)

Scheme 1 Insertion of [RP-$W(CO)_5$] into the P-H bond of secondary phosphine oxides

The insertion products **2** were characterized by NMR and HRMS. The ^{31}P NMR data are collected in table 1.

Table 1 ^{31}P NMR for compounds **2**

Product	$\delta^{31}P$	$^1J_{PP}$ (Hz)	$^1J_{PW}$ (Hz)	$^1J_{PH}$(Hz)
2a	34,0, -33.2	72.0	226.4	327.8
2b	34.2, -68.3	62.7	223.6	320.4
2c	34.7, -53.7	65.8	223.9	330.1
2d	34.1, -61.5	64.3	226.7	323.2
2e	34.4, -53.7	66.1	231.6	336.3
2f	21.0, -19.9	46.9	228.3	330.6
2g	20.7, -54.2	38.2	226.0	322.9

These data are very similar to those of the phosphonate analogues, the so-called phospha-Wittig reagents.[6] Compound **2a** was further characterized by X-ray crystal structure analysis (Fig. 1)

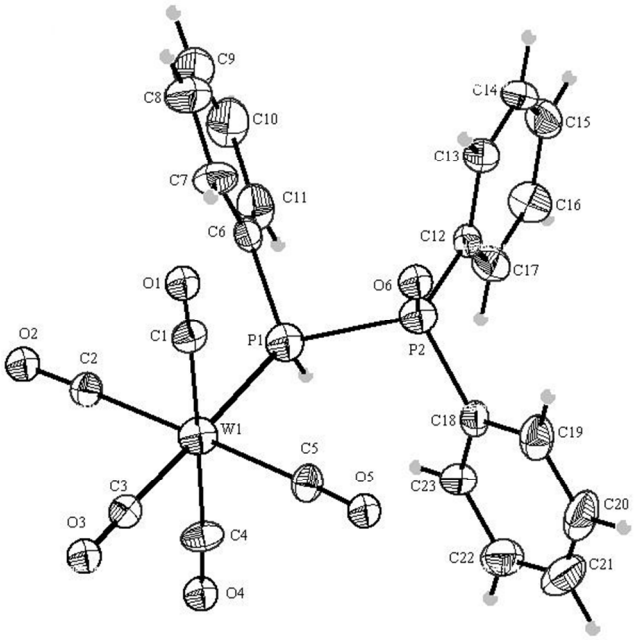


Fig. 1 X-ray crystal structure analysis of compound **2a**. Main bond lengths (Å) and angles (°): P1-P2 2.2081(18), P1-C6 1.824(5), P1-W1 2.5058(13), P2-O6 1.489(4), P2-C12 1.797(5), P2-C18 1.814(5); P2-P1-W1 113.54(6), C6-P1-W1 121.45(18), C6-P1-P2 100.97(16), C12-P2-C18 107.3(2), O6-P2-P1 109.97(17), O6-P2-C12 113.1(2), O6-P2-C18 113.8(3), C12-P2-P1 107.98(16), C18-P2-P1 104.14(18).

It is known that an easy tautomerism takes place between secondary phosphine oxides and phosphinic acids. The process is bimolecular and involves 6-membered transition states with activation barriers in the range 5-15 kcal mol^{-1}.[7] The key question concerning the mechanism of the insertion of phosphinidene complexes into the P-H bonds of secondary phosphine oxides is whether [RP-$W(CO)_5$] reacts with $Ar_2P(O)H$ or Ar_2P-OH. We have studied the interaction of [MeP-$W(CO)_5$] with $Ph_2P(O)H$ and Ph_2P-OH by DFT at the B3LYP/6-31G(d)-Lanl2dz (W) level.[8] We have not detected any interaction with the secondary phosphine oxide but a well defined P..O adduct is formed with the phosphinic acid (Fig. 2).

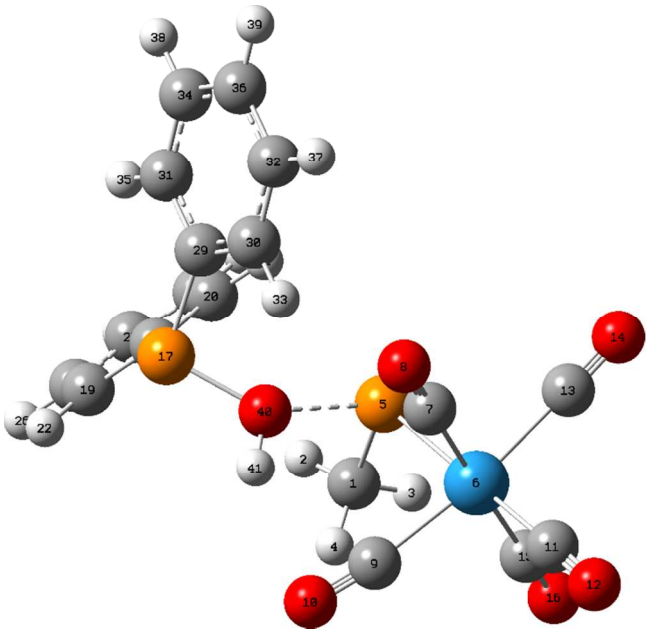
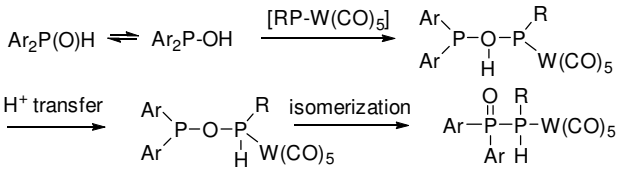


Fig. 2 Computed structure of the adduct [MeP-$W(CO)_5$]-$HOPPh_2$.Main bond lengths (Å) and angles (°): P5-O40 2.042, P17-O40 1.770, P5-C1 1.870, O40-H41 0.977; P5-O40-P17 136.06, P5-O40-H41 111.06, P17-O40-H41 109.89, C1-P5-O40-H41 66.96

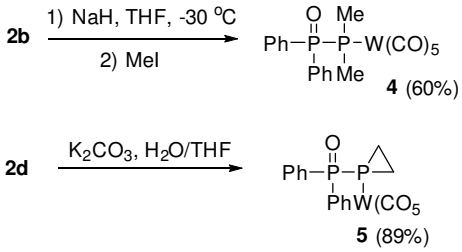
This adduct which corresponds to a local minimum (no negative frequency) is formed by the interaction of the phosphinidene LUMO with the in-plane lone pair of the hydroxyl oxygen. On this basis, we propose the mechanism depicted in Scheme 2 for the insertion of phosphinidenes into the P-H bonds:



Scheme 2 Insertion mechanism of [RP-$W(CO)_5$] into the P-H bond of $Ar_2P(O)H$

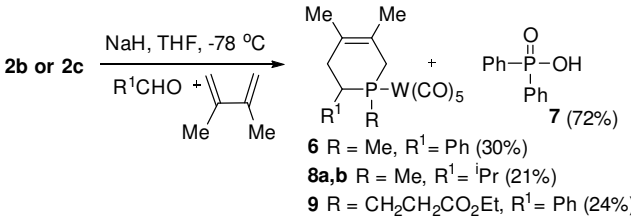
The first two steps are very similar to those proposed for the insertion of phosphinidene complexes into water.[2] When the diaryl is replaced by a dialkylphosphine oxide, the phosphinic acid tautomer becomes such a strong ligand that it becomes able to displace tungsten from the phosphinidene complex or from its precursor and the insertion fails. For example, with secondary di-n-butylphosphine oxide, the main product is ($^nBu_2POH$)$W(CO)_5$ (**3**) isolated in 41% yield.

It is possible to alkylate the PH bonds of the insertion products **2** as shown in Scheme 3:



Scheme 3 Alkylation of insertion products **2**

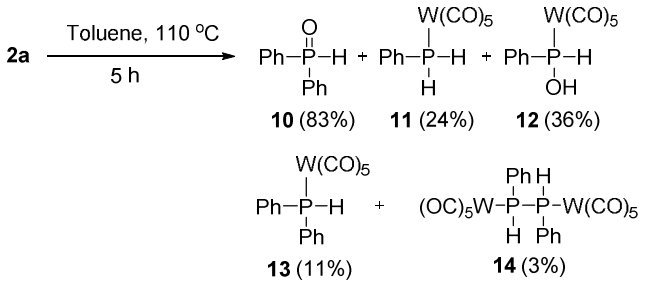
But the most interesting aspect of the chemistry of these insertion products is their use as phospha-Wittig reagents[9] for the conversion of carbonyl derivatives into P=C double bonds (Scheme 4):



Scheme 4 Compounds **2** as phospha-Wittig reagents

The phosphaalkene intermediates were trapped as [2+4] cycloadducts with dimethylbutadiene. Adducts **6** and **9** were obtained as single diastereomers but their stereochemistry was not determined.

Finally, a few words on the thermal stability of compounds **2** are appropriate. The experiments were performed with **2a**. Compound **2a** decomposes in boiling toluene to give a plethora of products (Scheme 5).



Scheme 5 Thermal decomposition of **2a**

The initial step of the decomposition seems to be the deinsertion of the phosphinidene from the P-H bond giving back the secondary phosphine oxide **10** in high yield. The suspected phosphinidene complex gives a variety of products **11**, **12** and **14**. **11** and **14** apparently come from the reaction of the phosphinidene with hydrogen[10] whose source is unknown. **12** and **13** probably arise from a H to OH exchange between the tautomer of **10** and **11**. Alternatively, the decomposition of **2a** could also occur via a bimolecular mechanism.

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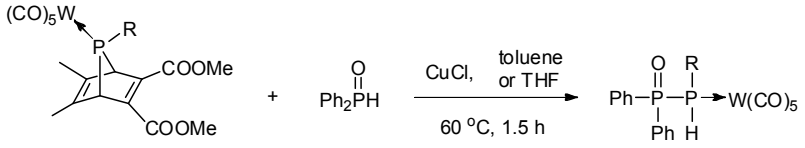
General Experimental Details

All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300 spectrometer. All spectra were recorded at 298 K in $CDCl_3$. All coupling constants (*J* values) are reported in Hertz (Hz). Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HR-MS spectrometer. Element analyses were performed on a Thermo Flash EA 1112 automatic element analyzer. IR spectra were obtained on a Thermo Nicolet is50 FT-IR spectrometer. X‑ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Silica gel (200-300 mesh) was used for the chromatographic separations. 7-phosphanorbornadiene complexes 1a, 1b, 1c, 1d, 1e were prepared according to literature methods. Commercially available reagents were used without further purification.

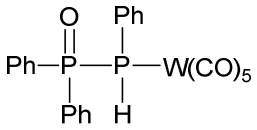
General procedure and characterization data for 2a-2e:



1a-1e **2a-2e**

	R	isolated yield of **2a-2e** (%)
a:	Ph	77
b:	Me	76
c:	CH2CH2COOEt	51
d:	CH_2CH_2Cl	52
e:	2-Th	45

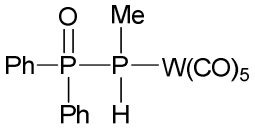
A solution of 7-R-7-phosphanorbornadiene complex **1a-1e**, diphenylphosphine oxide (1 eq) and CuCl (0.4 eq) in toluene or THF was stirred at 60 °C for 1.5 h. The solvents were removed *in vacuo*, and the residue was chromatographed at -15°C on silica gel using a 50:1 dichloromethane:THF mixture, to give a yellowish solid.

2a: 

7-phenyl-7-phosphanorbornadiene complex **1a** (2.57 g, 3.9 mmol). Yield: 1.91 g, 77 %. Single crystal for X-ray analysis was grown from a solution of the compound **2a** in dichloromethane

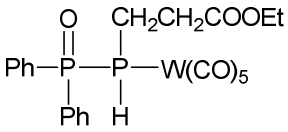
$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.0 (J_{PP} = 72.0 Hz, P^{V}), -33.2 (J_{PP} = 71.7 Hz, $^{1}J_{PW}$ = 226.4 Hz, $^{1}J_{PH}$ = 327.8 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 6.24 (dd, 1H, PH, J_{PH} = 326.7 Hz), 7.29-7.39 (m, 7H, Ph), 7.46-7.66 (m, 6H, Ph), 7.80-7.87 (m, 2H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 126.31 (d, J_{CP} = 35.6 Hz, C, Ph), 128.72 (d, J_{CP} = 12.3 Hz, CH, Ph), 128.99 (d, J_{CP} = 10.9 Hz, CH, Ph), 129.17 (d, J_{CP} = 12.2 Hz, CH, Ph), 129.92 (dd, $^{1}J_{CP}$ = 87.1 Hz, $^{2}J_{CP}$ = 14.9 Hz, C, Ph), 130.67 (dd, $^{1}J_{CP}$ = 87.1 Hz, $^{2}J_{CP}$ = 11.1 Hz, C, Ph), 131.02 (d, J_{CP} = 10.0 Hz, CH, Ph), 131.44 (d, J_{CP} = 9.7 Hz, CH, Ph), 132.64 (d, J_{CP} = 2.9 Hz, CH, Ph), 133.11 (d, J_{CP} = 2.6 Hz, CH, Ph), 133.64 (d, J_{CP} = 3.1 Hz, CH, Ph), 133.78 (d, J_{CP} = 3.1 Hz, CH, Ph), 194.88 (dd, J_{CP} = 6.4 Hz, J_{CP} = 1.4 Hz, J_{CW} = 126.8 Hz, CO *cis*), 197.48 (d, $^{2}J_{CP}$

= 25.3 Hz, CO *trans*). HRMS: m/z 635.0020 (calcd for $C_{23}H_{17}O_6P_2W$: $[M+H]^+$, 635.0010). IR (KBr) ν(CO) 2076 s, 1991s, 1909 vs cm^{-1}. Anal. Calcd for $C_{23}H_{16}O_6P_2W$: C, 43.56; H, 2.54. Found: C, 43.55; H, 2.41.

2b: 

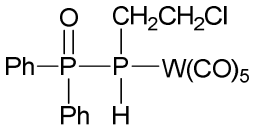
7-methyl-7-phosphanorbornadiene complex **1b** (1.20 g, 2.0 mmol). Yield: 0.93 g, 76 %.

^{31}P NMR ($CDCl_3$): δ 34.2 (J_{PP} = 62.7 Hz, P^V), -68.3 (J_{PP} = 63.0 Hz, $^1J_{PW}$ = 223.6 Hz, $^1J_{PH}$ = 320.4 Hz, P^{III}). ^1H NMR ($CDCl_3$): δ 1.74-1.82 (m, 3H, CH_3), 5.42 (dm, $^1J_{PH}$ = 320.6 Hz, 1H, PH), 7.58-7.65 (m, 6H, Ph), 7.83-7.92 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 7.39 (d, J_{CP} = 22.8 Hz, CH_3), 129.32 (d, J_{CP} = 12.3 Hz, CH, Ph), 129.97 (d, J_{CP} = 10.9 Hz, C, Ph), 130.52 (d, J_{CP} = 16.7 Hz, C, Ph), 131.06 (d, J_{CP} = 10.1 Hz, CH, Ph), 131.25 (d, J_{CP} = 9.7 Hz, CH, Ph), 133.06 (d, J_{CP} = 2.7 Hz, CH, Ph), 133.21 (d, J_{CP} = 2.3 Hz, CH, Ph), 194.89 (dd, $^2J_{CP}$ = 6.4 Hz, $^3J_{CP}$ = 1.2 Hz, $^1J_{CW}$ = 126.5 Hz, CO *cis*), 197.49 (d, $^2J_{CP}$ = 24.5 Hz, CO *trans*). HRMS: m/z 572.9852 (calcd for $C_{18}H_{15}O_6P_2W$: $[M+H]^+$, 572.9853). IR (KBr) ν(CO) 2075 s, 1992 w, 1912 vs cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_6P_2W$: C, 37.79; H, 2.47. Found: C, 37.79; H, 2.47.

Diphosphine monoxide **2c**: 

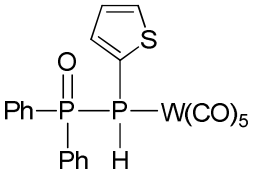
1c (3.9 g, 5.75 mmol). Yield: 1.39 g, 51 %.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.7 (J_{PP} = 65.8 Hz, P^{V}), -53.7 ppm (J_{PP} = 64.9 Hz, $^{1}J_{PW}$ = 223.9 Hz, $^{1}J_{PH}$ = 330.1 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, J_{HH} = 7.2 Hz, 3H, CH_3), 2.12-2.55 (dm, 2H, PCH_2), 2.57-2.72 (m, 2H, $CH_2C{=}O$), 4.12 (q, J_{HH} = 7.2 Hz, 2H, OCH_2), 5.60 (dm, $^{1}J_{PH}$ = 325.5 Hz, 1H, PH), 7.58-7.64 (m, 6H, Ph), 7.86-7.93 (m, 4H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 14.10 (s, CH_3), 18.24 (d, J_{CP} = 21.0 Hz, PCH_2), 31.07 (d, J_{CP} = 5.5 Hz, $\underline{C}H_2C{=}O$), 61.21 (s, OCH_2), 129.38 (d, J_{CP} = 12.2 Hz, CH, Ph), 129.43 (d, J_{CP} = 12.2 Hz, CH, Ph), 130.35 (d, J_{CP} = 9.7 Hz, C, Ph), 130.69 (d, J_{CP} = 16.7 Hz, C, Ph), 131.01 (d, J_{CP} = 10.1 Hz, CH, Ph), 131.21 (d, J_{CP} = 10.2 Hz, CH, Ph), 133.09 (d, J_{CP} = 2.9 Hz, CH, Ph), 133.27 (d, J_{CP} = 2.7 Hz, CH, Ph), 171.55 (d, J_{CP} = 8.4 Hz, C=O), 194.68 (dd, $^{2}J_{CP}$ = 6.4 Hz, $^{3}J_{CP}$ = 1.7 Hz, $^{1}J_{CW}$ = 124.7 Hz, CO *cis*), 196.82 (d, $^{2}J_{CP}$ = 24.8 Hz, CO *trans*). HRMS: m/z 659.0225 (calcd for $C_{22}H_{21}O_8P_2W$: $[M+H]^+$, 659.0221). IR (KBr) ν(CO) 2077 s , 1939 vs cm^{-1}.

Diphosphine monoxide **2d**: 

1d (580 mg, 0.9 mmol). Yield: 582 mg, 52 %.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.1 (J_{PP} = 64.3 Hz, P^{V}), -61.5 (J_{PP} = 64.3 Hz, $^{1}J_{PW}$ = 226.7 Hz, $^{1}J_{PH}$ = 323.2 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 2.34-2.78 (dm, 2H, PCH_2), 3.69-3.79 (m, 2H, CH_2Cl), 5.63 (dm, $^{1}J_{PH}$ = 322.8 Hz, 1H, PH), 7.59-7.66 (m, 6H, Ph), 7.85-7.94 (m, 4H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 27.05 (dd, $^{1}J_{CP}$ = 19.2 Hz, $^{2}J_{CP}$ = 2.2 Hz, PCH_2), 41.29 (d, $^{2}J_{CP}$ = 6.3 Hz, CH_2Cl), 129.47 (d, J_{CP} = 12.2 Hz, CH, Ph), 129.52 (d, J_{CP} = 12.3 Hz, CH, Ph), 130.20 (d, $^{2}J_{CP}$ = 10.0 Hz, C, Ph), 130.48 (d, $^{2}J_{CP}$ = 17.4 Hz, C, Ph), 130.98 (d, J_{CP} = 10.1 Hz, CH, Ph), 131.23 (d, J_{CP} = 9.1 Hz, CH, Ph), 133.27 (d, J_{CP} = 3.0 Hz, CH, Ph), 133.42 (d, J_{CP} = 2.5 Hz, CH, Ph), 194.54 (dd, $^{2}J_{CP}$ = 6.4 Hz, $^{3}J_{CP}$ = 1.7 Hz, $^{1}J_{CW}$ = 126.3 Hz, CO *cis*), 196.55 (d, $^{2}J_{CP}$ = 25.4 Hz, CO *trans*). HRMS: m/z 620.9609 (calcd for $C_{19}H_{16}ClO_6P_2W$: $[M+H]^{+}$, 620.9620).

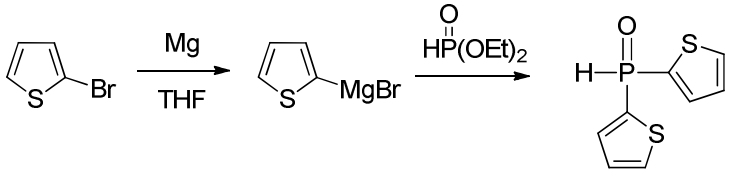
Diphosphine monoxide **2e**: 

1e(528 mg, 0.8 mmol). Yield: 210 mg, 45 %.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 34.4 (J_{PP} = 66.1 Hz, P^{V}), -53.7 (J_{PP} = 66.2 Hz, $^{1}J_{PW}$ = 231.6 Hz, $^{1}J_{PH}$ = 336.3 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 6.56 (dd, J_{PH} = 332.7 Hz, 1H, PH), 7.11-7.78 (m, 13H, Ph, Th). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 124.04 (d, $^{1}J_{CP}$ = 33.6 Hz, C, Th), 128.97 (d, J_{CP} = 12.5 Hz, CH, Ph), 129.15 (d, J_{CP} = 12.8 Hz, CH, Ph), 129.98 (d, $^{2}J_{CP}$ = 11.4 Hz, C, Ph), 130.15 (d, $^{2}J_{CP}$ = 14.3 Hz, C, Ph), 131.45 (d, J_{CP} = 9.8 Hz, CH, Ph), 131.65 (d, J_{CP} = 9.7 Hz, CH, Ph), 133.07 (d,

J_{CP} = 2.7 Hz, CH, Ph), 133.22 (d, J_{CP} = 2.8 Hz, CH, Ph), 133.93 (s, CH, Th), 138.25 (d, J_{CP} = 3.9 Hz, CH, Th), 138.37 (d, J_{CP} = 3.9 Hz, CH, Th), 194.78 (dd, $^{2}J_{CP}$ = 6.3 Hz, $^{3}J_{CP}$ = 1.3 Hz, $^{1}J_{CW}$ = 124.5 Hz, CO *cis*), 197.12 (d, $^{2}J_{CP}$ = 26.1 Hz, CO *trans*). HRMS: m/z 640.9575 (calcd for $C_{21}H_{15}O_6P_2SW$: $[M+H]^+$, 640.9574). IR (KBr) ν(CO) 2076 s, 1982 s, 1915 vs cm^{-1}. Anal. Calcd for $C_{21}H_{14}O_6P_2SW$: C, 39.40; H, 2.20; S, 5.01. Found: C, 39.14; H, 2.29; S, 4.90.

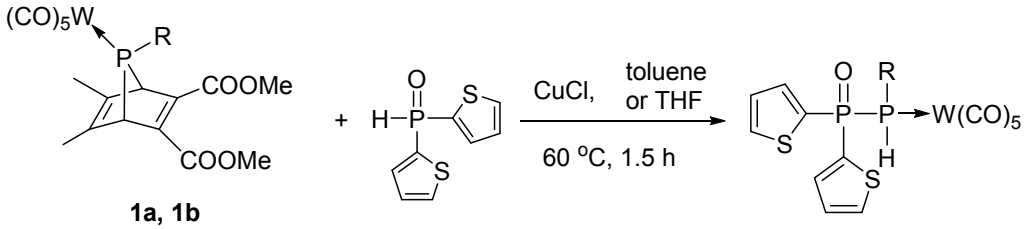
Procedure and characterization data for dithienylphosphine oxide:



A 100 mL Schlenk flask with 360 mg (15 mmol, 3.0 eq) Mg was evacuated/N_2 filled 3 times, then 10 mL dried THF and 0.2 mL 2-bromothiophene were added. After the initiation, 5 mL dried THF and 1.25 mL(15 mmol in total, 3.0 eq) 2-bromothiophene were added to the mixture. The mixture was stirred at ambient temperature for two hours and then cooled to -30 ^{o}C. A solution of diethylphosphite (0.64 mL, 5 mmol, 1.0 eq.) in 5 mL THF was then added dropwise over 15 minutes to the mixture. The mixture was kept 15 minutes at 0 ^{o}C, then the cold bath was removed, and the mixture stirred for two hours at ambient

temperature. 30 mL 0.3N HCl was added dropwise over 10 minutes at 0 ^{o}C, then 20 mL ethyl acetate was added to the mixture. The mixture was extracted with EtOAc and the organic phase was dried with $MgSO_4$, and then filtered through a Celite pad. Solvents were removed *in vacuo* to give 843 mg (79% yield) of dithienylphosphine oxide as a yellow oil. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -1.2 (J_{PH} = 515.4 Hz). ^{1}H NMR ($CDCl_3$): δ 7.22-7.25 (m, 2H, Th), 7.64-7.81 (m, 4H, Th), 8.46 (d, $^{1}J_{PH}$ = 515.4 Hz, 1H, PH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 128.48 (d, J_{CP} = 15.2 Hz, CH, Th), 131.78 (d, J_{CP} = 116.6 Hz, C, Th), 124.55 (d, J_{CP} = 5.6 Hz, CH, Th), 136.04 (d, J_{CP} = 12.4 Hz, CH, Th). HRMS: m/z 646.9139 (calcd for $C_{19}H_{13}O_6P_2S_2W$: $[M+H]^+$, 646.9138).

General procedure and characterization data for 2f, 2g:

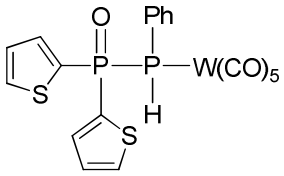


1a, 1b **2f, g**

	R	isolated yield of **3a, 3b** (%)
2f:	Ph	71
2g:	Me	40

A solution of 7-R-7-phosphanorbornadiene complex **1a-1b** (0.8 mmol, 1eq), dithienylphosphine oxide (0.8 mmol, 1eq) and CuCl (0.3 mmol) in toluene or THF (10 mL) was stirred at 60 °C for 1.5 h. The solvents were

removed *in vacuo*, and the residue was chromatographed at -15°C on silica gel using a 50:1 dichloromethane:THF mixture, to give a yellowish solid.

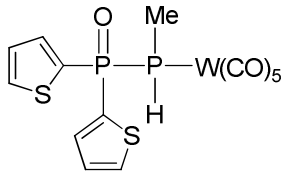


2f:

463 mg, 71 %.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 21.0 (J_{PP} = 46.9 Hz, P^{V}), -19.9 (J_{PP} = 46.9 Hz, $^{1}J_{PW}$ = 228.3 Hz, $^{1}J_{PH}$ = 330.6 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 6.19 (dd, $^{1}J_{PH}$ = 330.3 Hz, $^{2}J_{PH}$ = 2.7 Hz, 1H, PH), 7.10 (s, 1H, Ph), 7.26-7.43 (m, 7H, Ph, Th), 7.67-7.74 (m, 2H, Ph), 7.84-7.86 (m, 1H, Th). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 126.48 (d, $^{1}J_{CP}$ = 35.2 Hz, C, Ph), 128.64 (d, J_{CP} = 14.5 Hz, CH, Ph), 128.99 (d, J_{CP} = 14.6 Hz, CH, Ph), 129.02(d, J_{CP} = 1.7 Hz, CH, Th), 129.15 (d, J_{CP} = 1.6 Hz, CH, Th), 130.27 (dd, $^{1}J_{CP}$ = 99.6 Hz, $^{2}J_{CP}$ = 17.1 Hz, C, Th), 130.62 (dd, $^{1}J_{CP}$ = 100.9 Hz, $^{2}J_{CP}$ = 15.7 Hz, C, Th), 131.42 (t, CH, Ph), 133.62 (d, J_{CP} = 3.6 Hz, CH, Ph), 133.76 (d, J_{CP} = 3.5 Hz, CH, Ph), 135.16 (d, J_{CP} = 4.7 Hz, CH, Th), 135.36 (d, J_{CP} = 4.6 Hz, CH, Th), 137.15 (d, J_{CP} = 10.0 Hz, CH, Th), 137.47 (d, J_{CP} = 9.9 Hz, CH, Th), 194.70 (dd, $^{2}J_{CP}$ = 6.6 Hz, $^{3}J_{CP}$ = 2.0 Hz, $^{1}J_{CW}$ = 127.5 Hz, CO *cis*), 197.42 (d, $^{2}J_{CP}$ = 25.5 Hz, CO *trans*). HRMS: m/z 646.9139 (calcd for $C_{19}H_{13}O_6P_2S_2W$: $[M+H]^+$, 646.9138). IR (KBr) ν(CO) 2077 s, 1991 s, 1940 vs, 1913 vs cm^{-1}. Anal. Calcd for $C_{19}H_{12}O_6P_2S_2W$: C,

35.31; H, 1.87; S, 9.92. Found: C, 35.38; H, 1.90; S, 9.71.

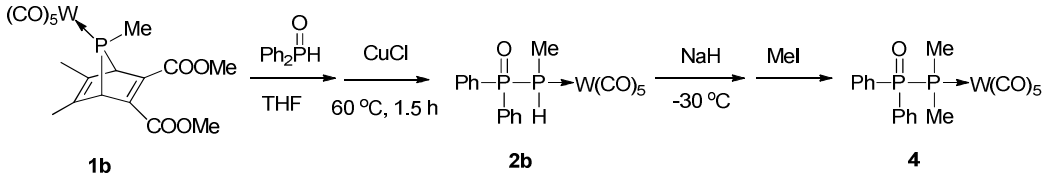


2g:

182 mg, 40 %.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 20.7 (J_{PP} = 38.2 Hz, P^{V}), -54.2 (J_{PP} = 38.0 Hz, $^{1}J_{PW}$ = 226.0 Hz, $^{1}J_{PH}$ = 322.9 Hz, P^{III}). ^{1}H NMR ($CDCl_3$): δ 1.81-1.89 (m, 3H, CH_3), 5.40 (dm, $^{1}J_{PH}$ = 323.1 Hz, 1H, PH), 7.32 (s, 2H, Th), 7.79-7.90 (m, 4H, Th). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 8.19 (d, J_{CP} = 22.0 Hz, CH_3), 129.13 (d, J_{CP} = 14.5 Hz, CH, Th), 129.84 (dd, $^{1}J_{CP}$ = 102.5 Hz, $^{2}J_{CP}$ = 18.9 Hz, C, Th), 130.37 (dd, $^{1}J_{CP}$ = 100.5 Hz, $^{2}J_{CP}$ = 15.3 Hz, C, Th), 135.50 (d, J_{CP} = 4.8 Hz, CH, Th), 135.67 (d, J_{CP} = 4.5 Hz, C, Th), 137.41 (d, J_{CP} = 10.0 Hz, CH, Th), 137.71 (d, J_{CP} = 10.0 Hz, CH, Th), 194.74 (dd, $^{2}J_{CP}$ = 6.6 Hz, $^{3}J_{CP}$ = 2.0 Hz, $^{1}J_{CW}$ = 125.1 Hz, CO *cis*), 197.40 (d, $^{2}J_{CP}$ = 25.0 Hz, CO *trans*). HRMS: m/z 584.8974 (calcd for $C_{14}H_{11}O_6P_2S_2W$: $[M+H]^+$, 584.8982). IR (KBr) ν(CO) 2077 s, 1991 s, 1910 vs cm^{-1}. Anal. Calcd for $C_{14}H_{10}O_6P_2S_2W$: C, 28.79; H, 1.73; S, 10.98. Found: C, 28.75; H, 1.71; S, 10.83.

Procedure and characterization data for compound 4:

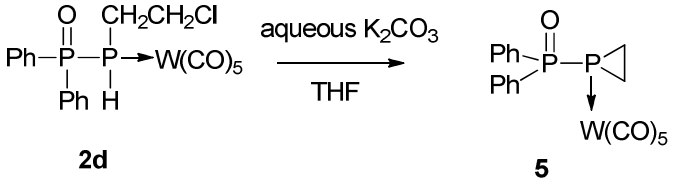


A solution of 7-Me-7-phosphanorbornadiene complex **1b** (300 mg, 0.5 mmol), diphenylphosphine oxide (105 mg, 0.5 mmol) and CuCl (25mg, 0.25 mmol) in THF (10 mL) was stirred at 60 °C for 1.5 h. Then NaH (60%, 20 mg, 0.5 mmol) was added at -30°C, the mixture was stirred at ambient temperature for 30 min. MeI (40 μL, 0.6 mmol) was added to the mixture at ambient temperature and stirred for 20 min. The solvents were removed *in vacuo*. A light yellow solid (140 mg, 60 %) was recovered by TLC using DCM as the eluent.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 35.3 (J_{PP} = 78.7 Hz, P^V), -33.6 (J_{PP} = 78.6 Hz, $^{1}J_{PW}$ = 228.2 Hz, P^{III}),. ^{1}H NMR ($CDCl_3$): 1.83 (dd, J_{PH} = 2.5Hz, J_{PH} = 1.6Hz, CH_3), 7.57-7.67 (m, 6H, Ph), 7.83-7.90 (m, 4H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 15.75 (dd, $^{1}J_{CP}$ = 22.2 Hz, $^{2}J_{CP}$ = 1.6 Hz, CH_3), 129.16 (d, J_{CP} = 12.0 Hz, CH, Ph), 129.37 (dd, $^{1}J_{CP}$ = 86.6 Hz, $^{2}J_{CP}$ = 14.0 Hz, C, Ph), 131.75 (dd, J_{CP} = 9.6 Hz, J_{CP} = 1.0 Hz, CH, Ph), 133.09 (d, J_{CP} = 2.6 Hz, CH, Ph), 195.96 (d, $^{2}J_{CP}$ = 6.6 Hz, $^{1}J_{CW}$ = 124.9 Hz, CO *cis*), 198.15 (d, $^{2}J_{CP}$ = 23.1 Hz, CO *trans*). HRMS: m/z 587.0005 (calcd for $C_{19}H_{16}O_6P_2W$: $[M+H]^+$, 587.0004). IR (KBr) ν(CO) 2074 w, 1983 w, 1933 vs, 1912 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_6P_2W$: C,

38.93; H, 2.75. Found: C, 38.91; H, 2.71.

Procedure and characterization data for compound 5:



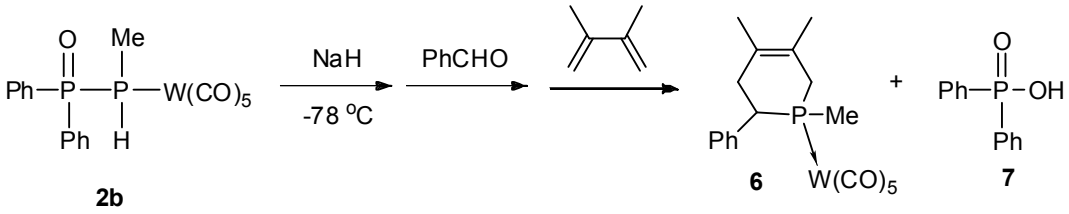
2d **5**

Aqueous K_2CO_3 (4 mL, 0.2 mol/L) was added dropwise to a solution of **2d** (139 mg, 0.22 mmol) in THF (3 mL) at r. t. and stirred for 10 min. The mixture was extracted with Et_2O and the solvents were removed *in vacuo.* The residue was chromatographed at -15°C on silica gel using a 50:1 dichloromethane:THF mixture, to give a yellowish solid (114 mg, 89 %).

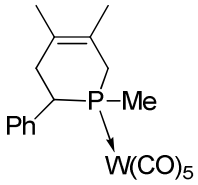
$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.8 (J_{PP} = 129.4 Hz, P^V), -226.0 (J_{PP} = 129.2 Hz, $^1J_{PW}$ = 240.1 Hz, P^{III}),. ^1H NMR ($CDCl_3$): 1.54-1.61 (m, 2H, CH_2), 2.15-2.24 (m, 2H, CH_2), 7.57-7.68 (m, 6H, Ph), 7.80-7.86 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.79 (d, $^1J_{CP}$ = 18.8 Hz, CH_2), 129.29 (d, J_{CP} = 12.5 Hz, CH, Ph), 129.74 (dd, $^1J_{CP}$ = 92.5 Hz, $^2J_{CP}$ = 16.8 Hz, C, Ph), 131.95 (dd, J_{CP} = 10.4 Hz, J_{CP} = 2.3 Hz, CH, Ph), 133.26 (d, J_{CP} = 2.6 Hz, CH, Ph), 194.70 (d, $^2J_{CP}$ = 7.2 Hz, $^1J_{CW}$ = 125.8 Hz, CO *cis*), 196.03 (dd, $^2J_{CP}$ = 33.0 Hz, $^3J_{CP}$ = 2.9 Hz, CO *trans*). HRMS: m/z 584.9850 (calcd for $C_{19}H_{15}O_6P_2W$: $[M+H]^+$, 584.9853).

IR (KBr) ν(CO) 2076 s, 1917 vs cm^{-1}. Anal. Calcd for $C_{19}H_{14}O_6P_2W$: C, 39.07; H, 2.42. Found: C, 39.17; H, 2.31.

Procedure and characterization data for compound 6:



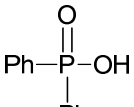
PhCHO (55 μL, 0.5 mmol), and excess of 2,3-dimethyl-1,3-butadiene (565 μL, 5 mmol) was added to a solution of **2b** (286 mg, 0.5 mmol) in THF (8 mL) successively. Then NaH (20 mg, 0.5 mmol) was added to the solution at − 78 °C and stirred at room temprature for 10 min. The solvents were removed in *vacuo.* The residue was washed with THF to give **7** (78 mg, 72 %) as a white solid. Then the residue was chromatographed on silica gel using petroleum ether to give **6** as a yellowish oil (81mg, 30 %).



6

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -17.9 (J_{PW} = 239.6 Hz). ^1H NMR ($CDCl_3$): 1.61 (d, $^2J_{PH}$ = 6.6 Hz, 3H, CH_3P), 1.74 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 2.44-2.58 (m, 2H, CH_2), 2.65-2.81 (m, 2H, CH_2), 3.09-3.18 (m, 1H, CH), 7.25-7.33 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.57 (d, $^1J_{CP}$ = 25.0 Hz, CH_3P), 20.14 (d, J_{CP} = 1.5 Hz, CH_3), 21.57 (d, J_{CP} = 8.1 Hz, CH_3), 36.51 (s, CH_2), 37.71 (d, $^1J_{CP}$ =

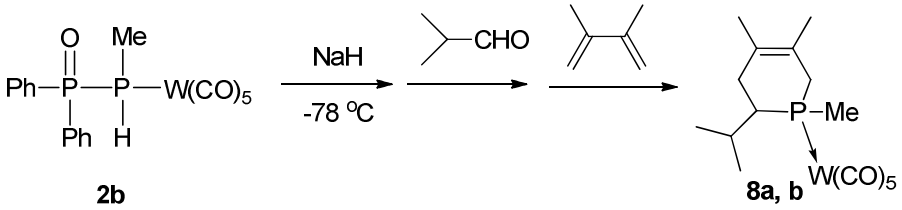
25.1 Hz, CH_2P), 44.0 (d, $^1J_{CP}$ = 21.7 Hz, CHP), 121.33 (d, J_{CP} = 4.1 Hz, =C-), 127.52 (d, J_{CP} = 3.0 Hz, CH, Ph), 128.08 (d, J_{CP} = 9.4 Hz, =C-), 128.31 (d, J_{CP} = 4.8 Hz, CH, Ph), 128.83 (d, J_{CP} = 2.4 Hz, CH, Ph), 138.86 (d, J_{CP} = 0.7 Hz, C, Ph), 196.70 (d, J_{CP} = 7.2 Hz, CO *cis*), 198.98 (d, J_{CP} = 21.5 Hz, CO *trans*).



7

$^{31}P\{^1H\}$ NMR (CD_3OD): δ 20.63. ^1H NMR (CD_3OD): δ 5.07 (s, 1H), 7.35-7.38 (m, 6H, Ph), 7.77-7.84 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 127.49 (d, J_{CP} = 12.1 Hz, CH, Ph), 129.65 (d, J_{CP} = 2.2 Hz, CH, Ph *para*), 130.91 (d, J_{CP} = 9.4 Hz, CH, Ph), 139.41 (d, J_{CP} = 131.7 Hz, C, Ph *ipso*).

Procedure and characterization data for compound 8a,b:



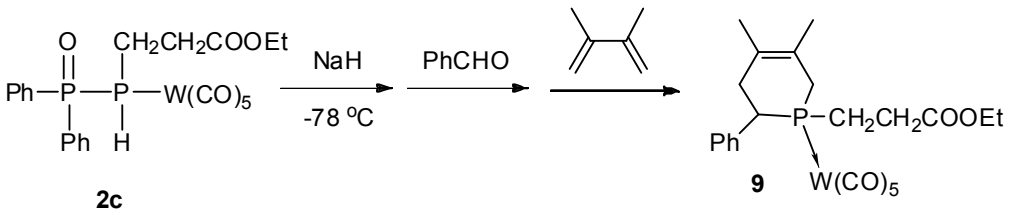
2b **8a, b**

Isobutyraldehyde (46 µL, 0.5 mmol), and excess of 2,3-dimethyl-1,3-butadiene (565 µL, 5 mmol) was added to a solution of **2b** (286 mg, 0.5 mmol) in THF (8 mL) successively. Then NaH (20 mg, 0.5 mmol) was added to the solution at − 78 °C and stirred at room temperature for 10 min. The solvents were removed in *vacuo.* The residue was chromatographed on silica gel using petroleum ether to give a mixture of **8a, b** as a yellowish solid (53 mg, 21 %, **8a**:**8b** = 1:0.8).

8a: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -22.4 (J_{PW} = 230.8 Hz). ^{1}H NMR ($CDCl_3$): 0.90 (d, J = 6.9 Hz, 3H, CH_3), 1.10 (d, J = 2.7 Hz, 3H, CH_3), 1.53 (d, J = 6.9 Hz, 3H, CH_3), 1.66-1.72 (m, 6H,CH_3), 1.77-1.79 (m, 1H, CH), 2.03-2.20 (m, 2H, CH_2), 2.28-2.50 (m, 3H, CH + CH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 12.55 (d, $^{1}J_{CP}$ = 23.0 Hz, CH_3P), 17.50 (d, J_{CP} = 1.7 Hz, CH_3), 20.43 (s, CH_3), 21.11 (d, J_{CP} = 8.2 Hz, CH_3), 22.56 (d, J_{CP} = 14.6 Hz, CH_3), 29.76 (d, J_{CP} = 4.4 Hz, CH), 35.14 (s, CH_2), 38.83 (d, $^{1}J_{CP}$ = 29.2 Hz, CH_2P), 40.14 (d, $^{1}J_{CP}$ = 24.2 Hz, CHP), 121.13 (d, J_{CP} = 8.0 Hz, =C-), 126.91 (d, J_{CP} = 7.0 Hz, =C-), 197.11 (d, J_{CP} = 7.2 Hz, CO *cis*), 199.55 (d, J_{CP} = 19.8 Hz, CO *trans*).

8b: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ-23.4 (J_{PW} = 230.1 Hz). ^{1}H NMR ($CDCl_3$): 1.04 (d, J = 6.6 Hz, 3H, CH_3), 1.07 (d, J = 2.7 Hz, 3H, CH_3), 1.61 (d, J = 6.6 Hz, 1H, CH), 1.66-1.72 (m, 9H,CH_3), 1.87-1.94 (m, 1H, CH), 2.03-2.20 (m, 2H, CH_2), 2.63-2.79 (m, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 19.83 (d, J_{CP} = 1.7 Hz, CH_3), 20.03 (s, CH_3), 20.89 (d, $^{1}J_{CP}$ = 24.7 Hz, CH_3P), 21.29 (d, J_{CP} = 1.8 Hz, CH_3), 23.82 (d, J_{CP} = 6.6 Hz, CH_3), 27.62 (d, J_{CP} = 6.4 Hz, CH_2), 31.52 (d, J_{CP} = 3.5 Hz, CH), 38.56 (d, $^{1}J_{CP}$ = 29.0 Hz, CH_2P), 40.41 (d, $^{1}J_{CP}$ = 22.2 Hz, CHP), 120.87 (d, J_{CP} = 3.8 Hz, =C-), 128.08 (d, J_{CP} = 10.9 Hz, =C-), 196.95 (d, J_{CP} = 7.1 Hz, CO *cis*), 198.97 (d, J_{CP} = 20.1 Hz, CO *trans*).

Procedure and characterization data for compound 9:

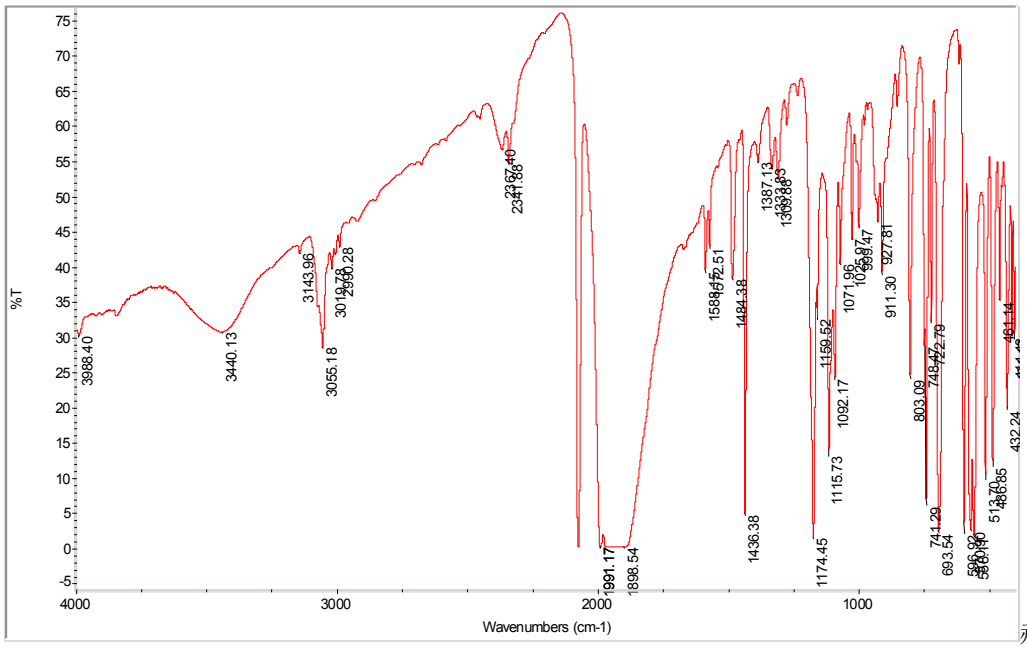


2c **9**

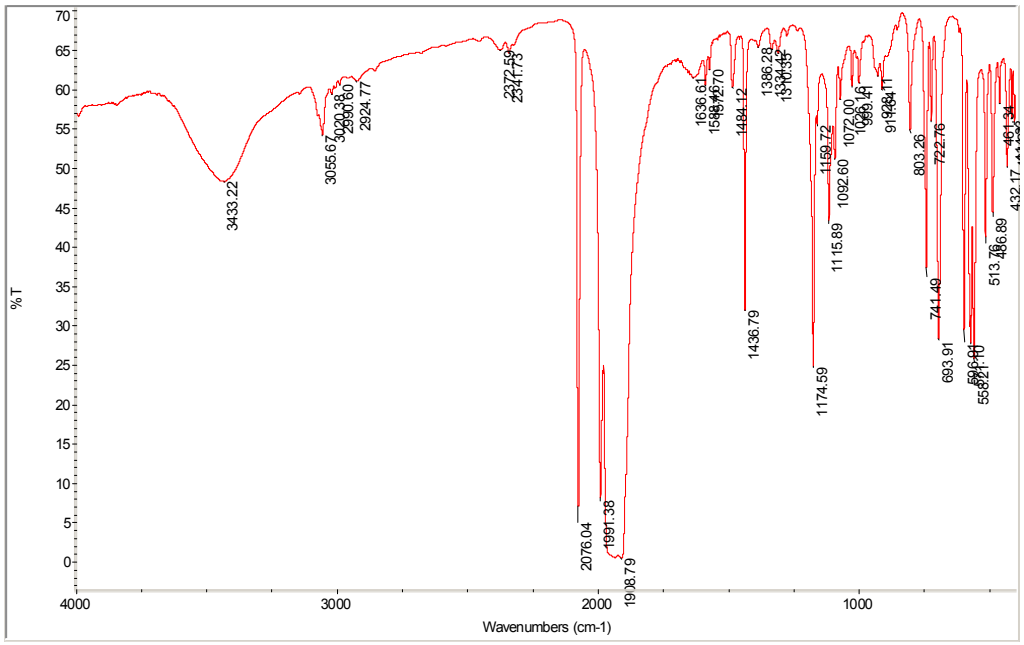
PhCHO (100 μL, 1.0 mmol), and excess of 2,3-dimethyl-1,3-butadiene (1.13 mL, 10 mmol) was added to a solution of **2c** (658 mg, 1 mmol) in THF (10 mL) successively. Then NaH (40 mg, 1 mmol) was added to the solution at − 78 °C and stirred at room temperature for 10 min. The solvents were removed in *vacuo.* The residue was chromatographed on silica gel using petroleum ether/ ethyl acetate 10:1 to give a yellowish oil (152mg, 24%).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -7.4 (J_{PW} = 243.4 Hz). ^{1}H NMR ($CDCl_3$): 1.25 (t, J_{HH} = 7.2 Hz, 3H, CH_3 Et), 1.73 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 2.10-2.74 (m, 8H, CH_2), 3.14-3.23 (m, 1H, CH), 4.14 (q, J_{HH} = 6.9 Hz, 2H, CH_2 Et), 7.24-7.32 (m, 5H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 14.16 (s, CH_3), 20.09 (d, J_{CP} = 1.1 Hz, CH_3), 21.65 (d, J_{CP} = 7.6 Hz, CH_3), 26.58 (d, J_{CP} = 23.2 Hz, CH_2), 29.36 (d, J_{CP} = 2.5 Hz, CH_2), 34.95 (d, J_{CP} = 24.1 Hz, CH_2), 36.91 (s, CH_2), 42.11 (d, J_{CP} = 20.4 Hz, CHP), 61.06 (s, CH_2), 121.40 (d, J_{CP} = 4.8 Hz, =C-), 127.73 (d, J_{CP} = 2.8 Hz, CH, Ph), 128.11 (d, J_{CP} = 9.2 Hz, =C-), 128.37 (d, J_{CP} = 4.8 Hz, CH, Ph), 129.04 (d, J_{CP} = 2.1 Hz, CH, Ph), 139.52 (s, C, Ph), 172.10 (d, J_{CP} = 14.8 Hz, C=O), 196.43 (d, J_{CP} = 7.0 Hz, CO *cis*), 198.14 (d, J_{CP} = 22.2 Hz, CO *trans*).

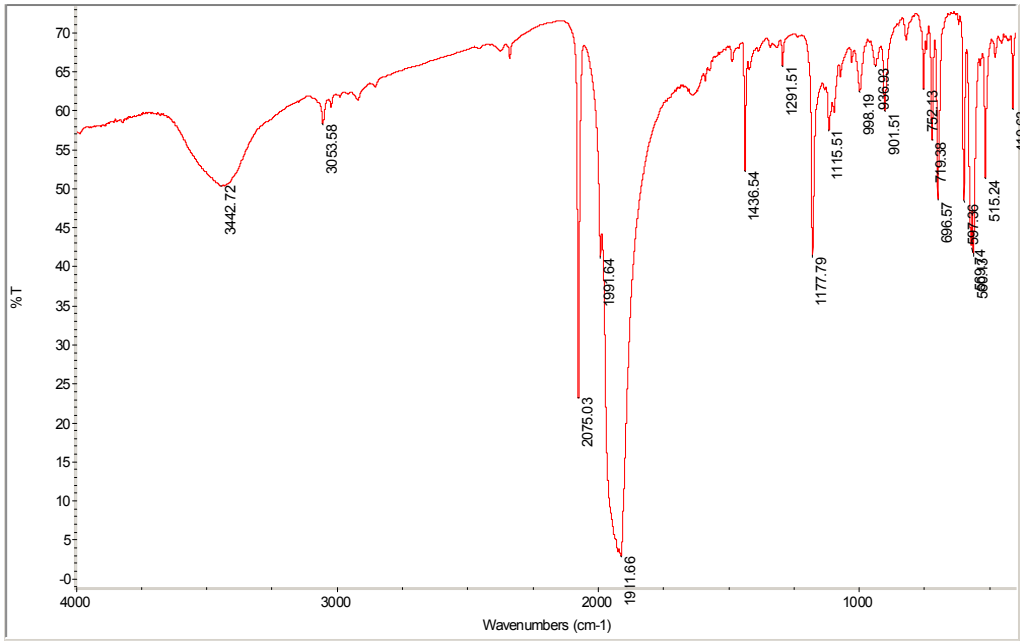
Compound 2a



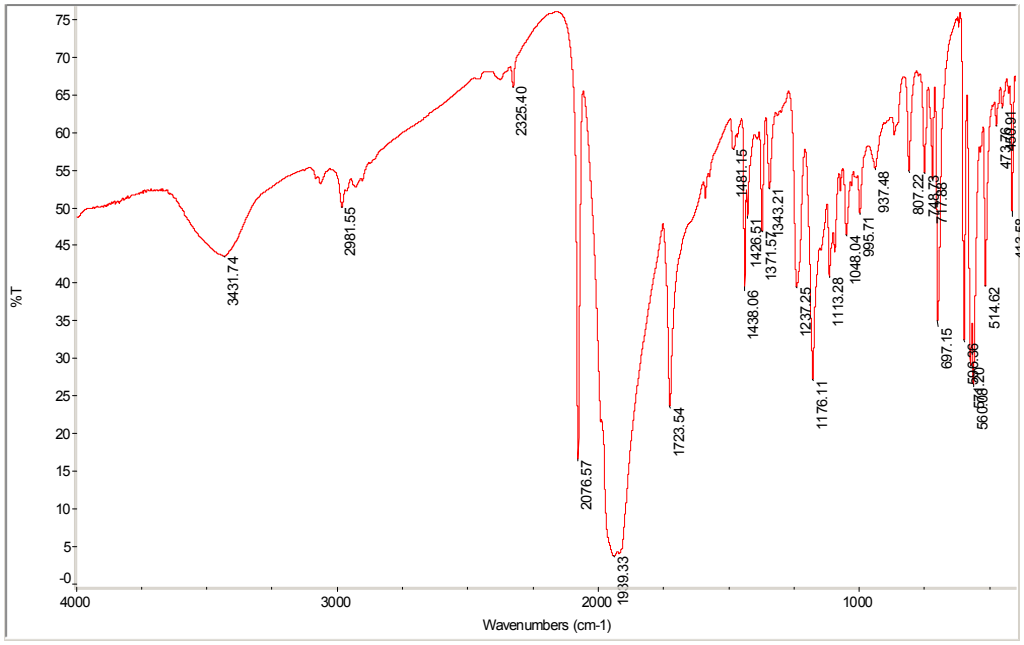
Compound 2a-2



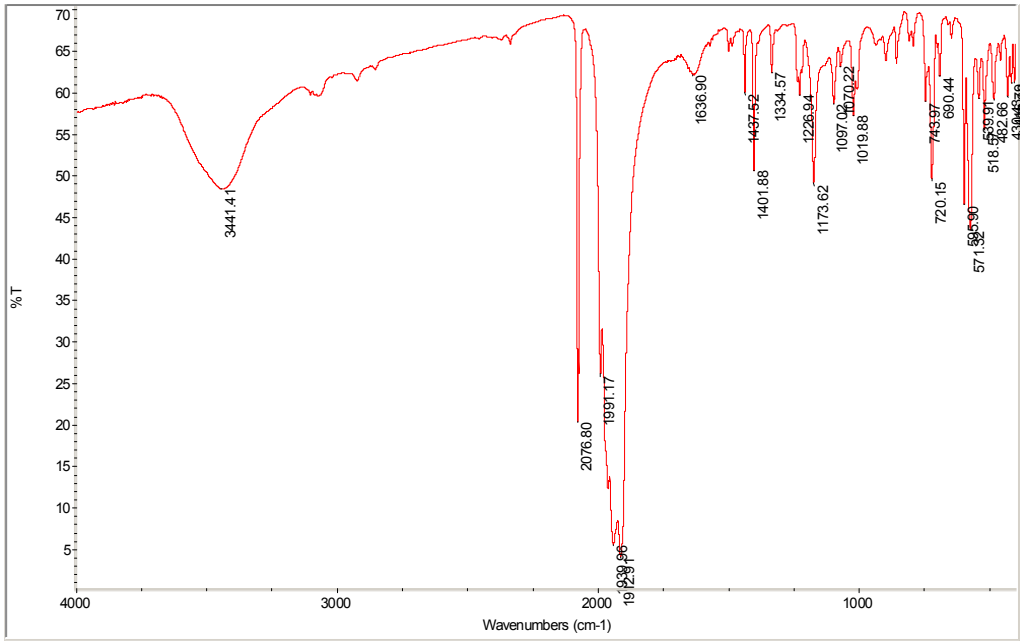
Compound 2b



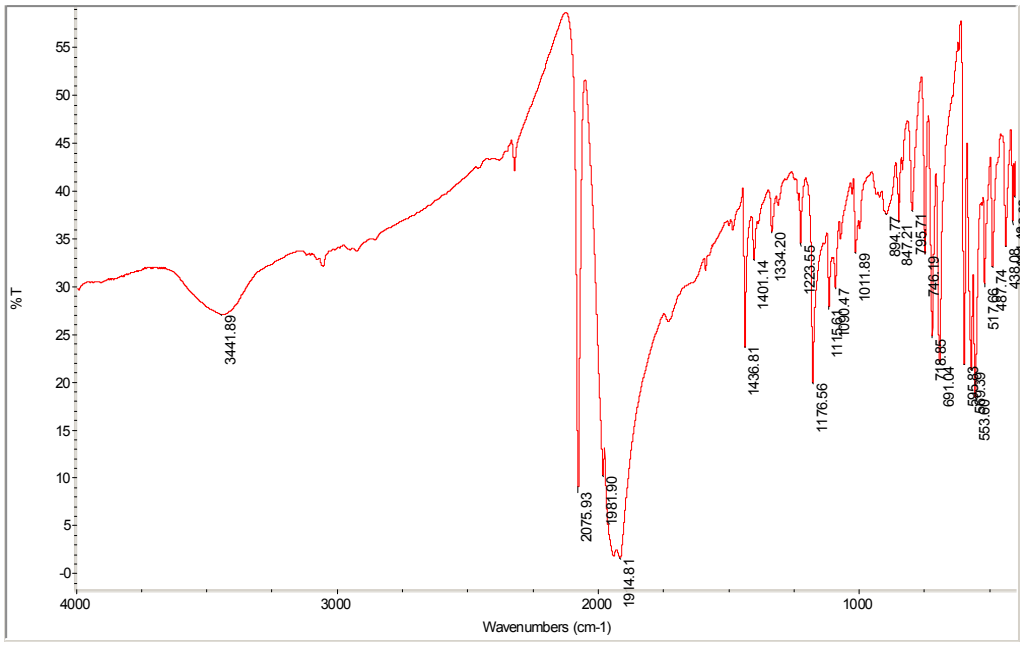
Compound 2c



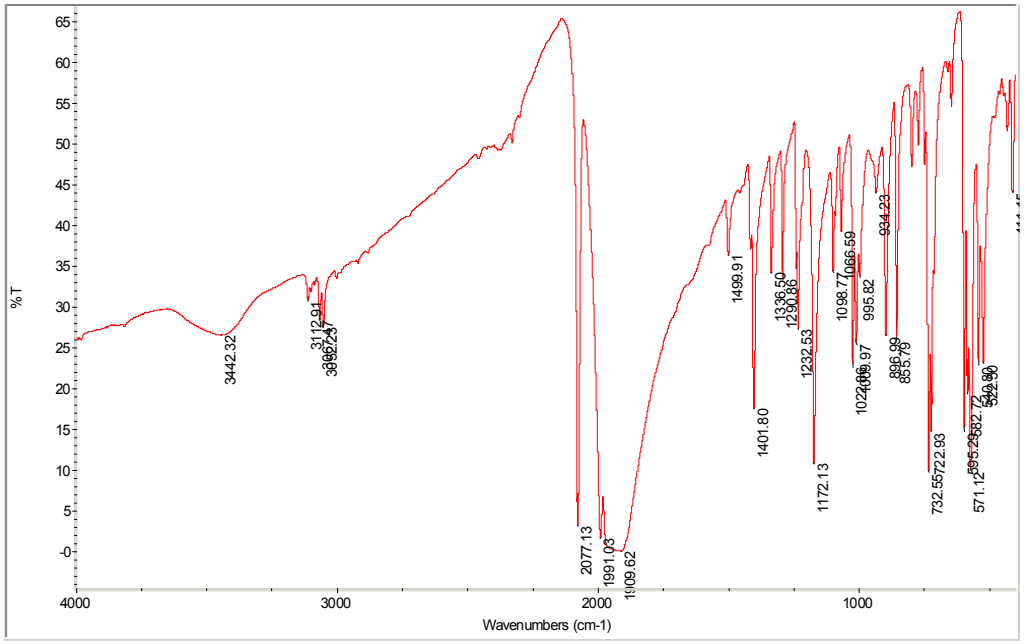
Compound 2f



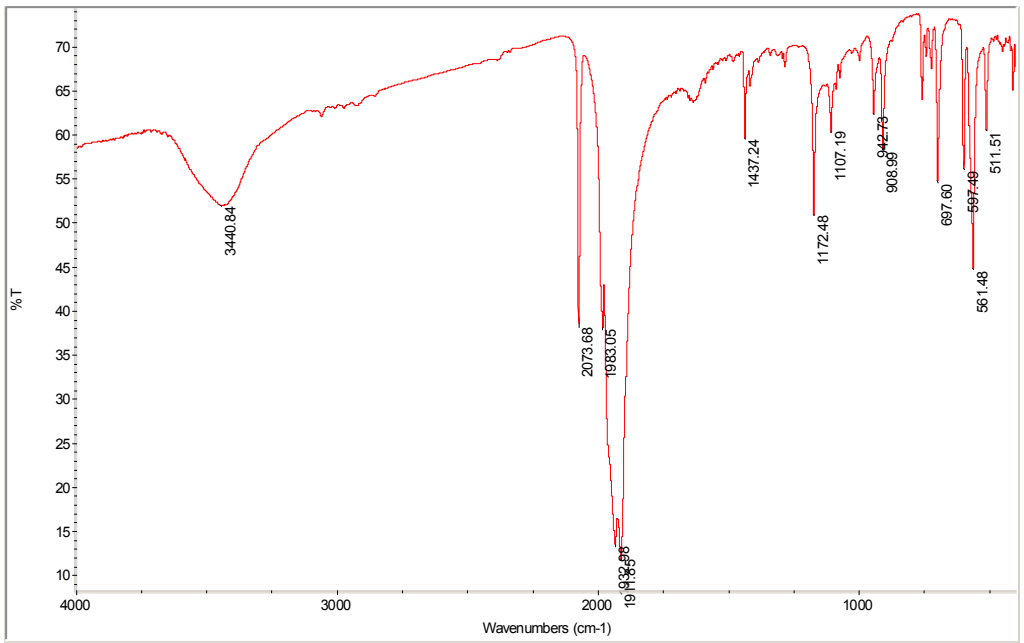
Compound 2e



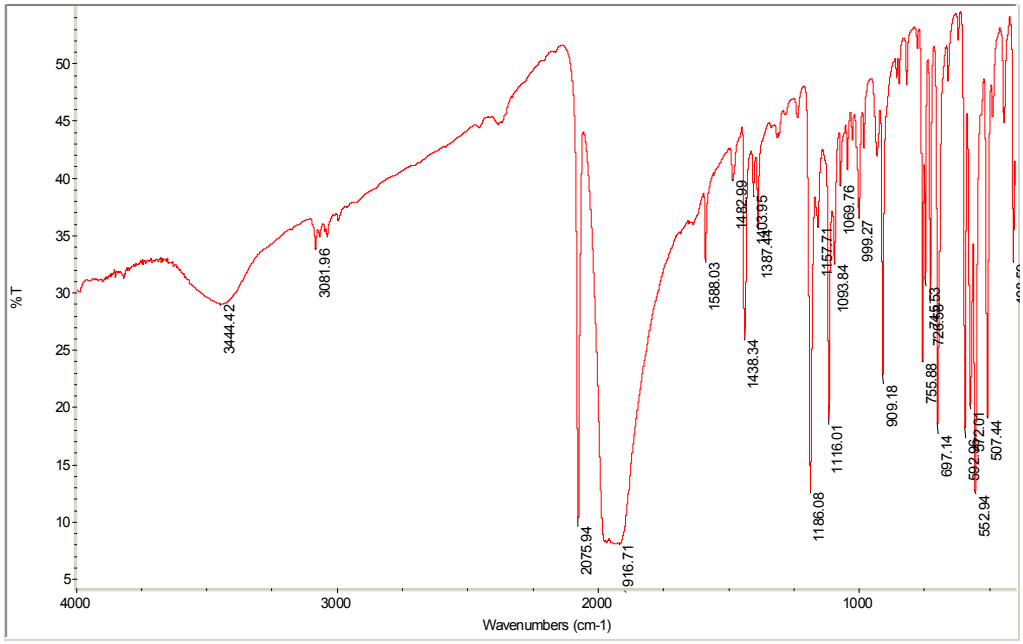
Compound 2g



Compound 4



Compound 5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20
15
10
5
4000
3000
2000
1000
Wavenumbers (cm-1)
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3081.96
2075.94
916.71
1588.03
1482.99
1438.34
1387.44
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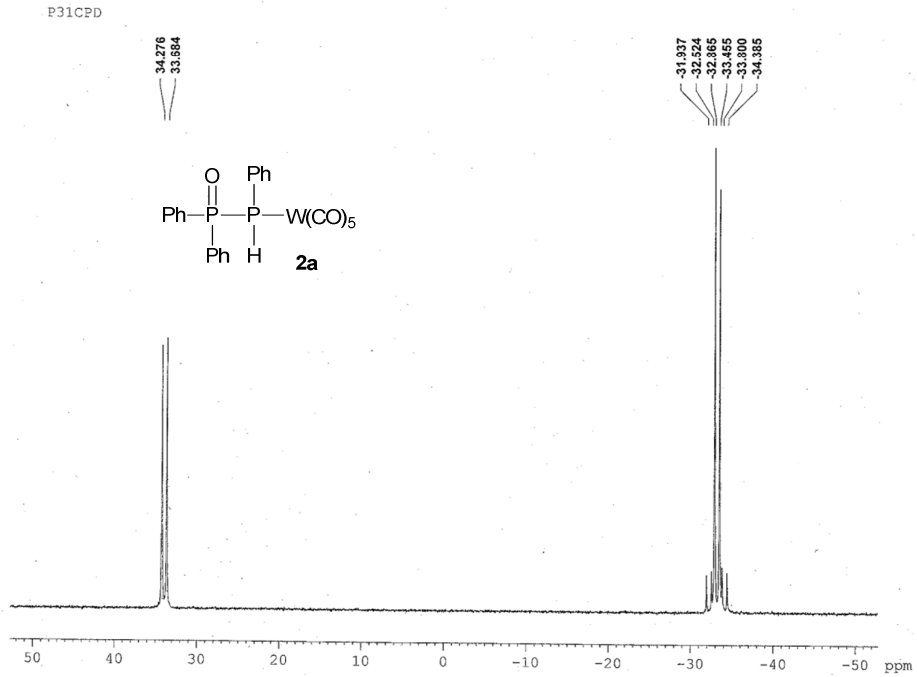
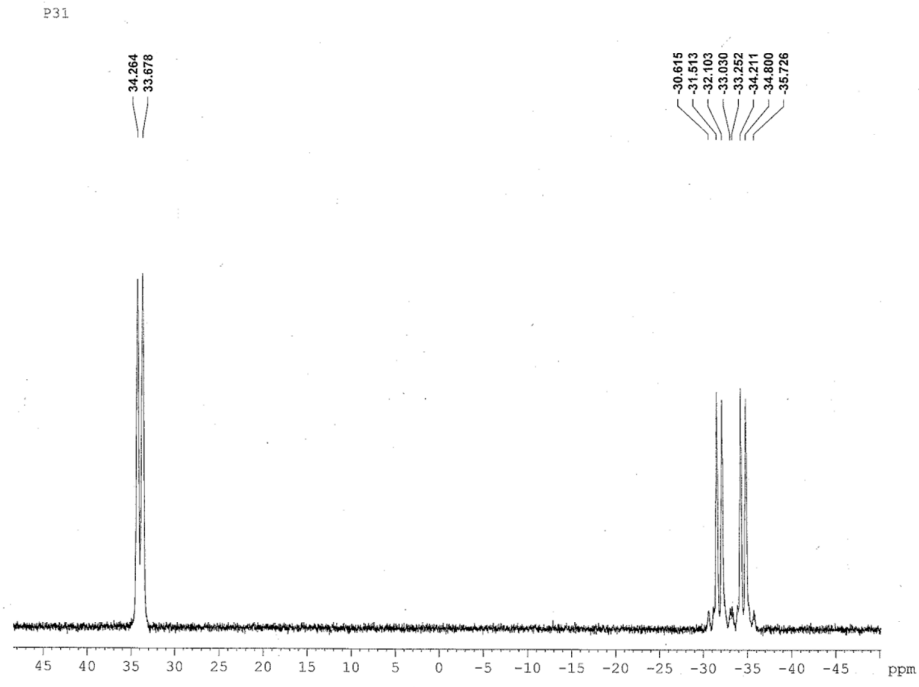
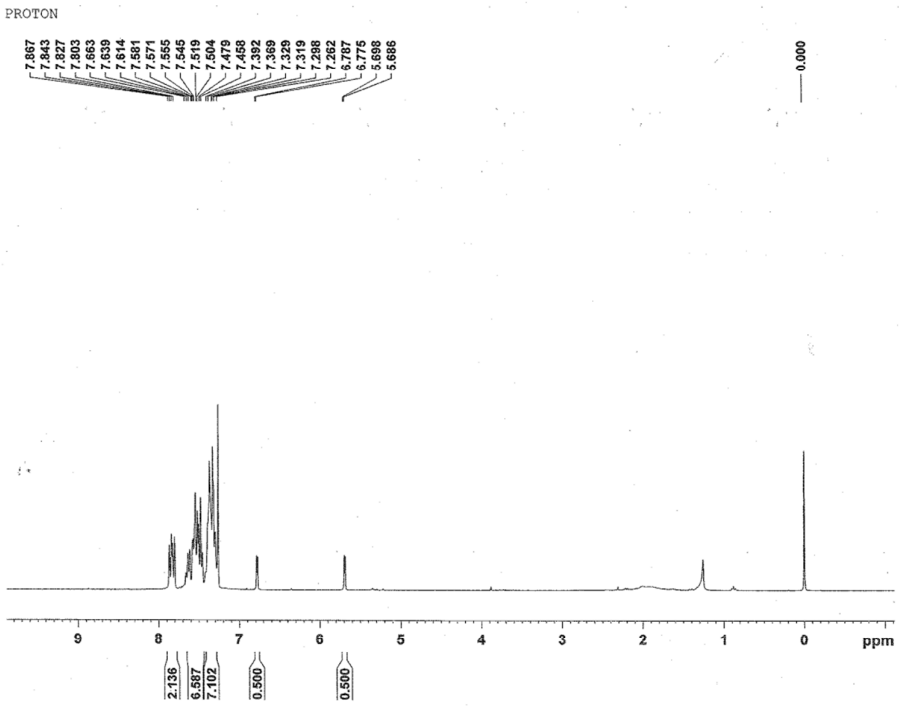
1116.01
1093.84
1069.76
999.27
909.18
755.88
697.14
552.94
507.44



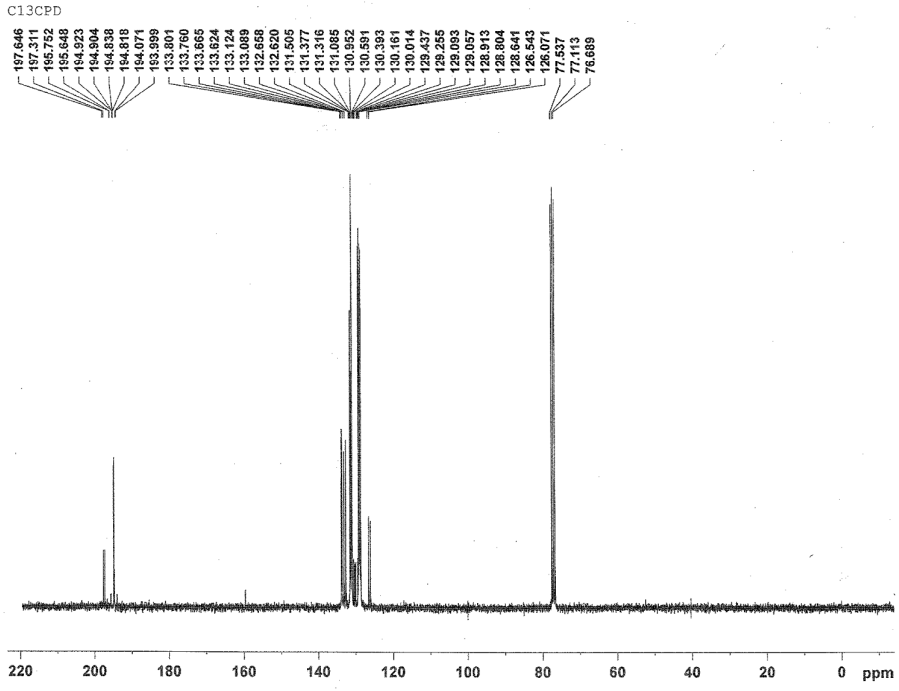
^{31}P CPD NMR ($CDCl_3$) of **2a**



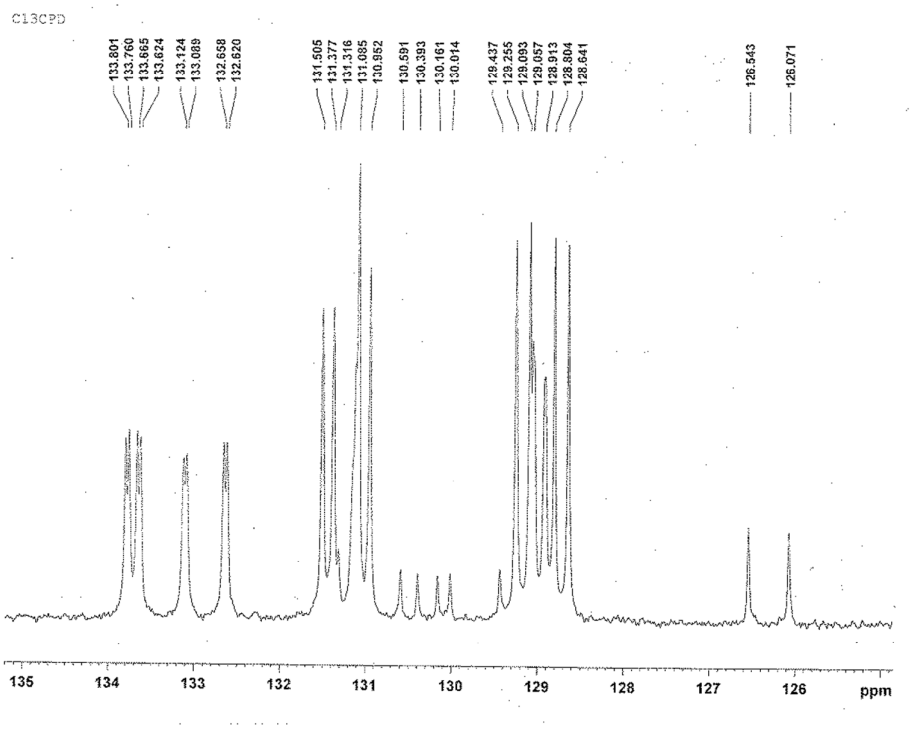
^{31}P NMR ($CDCl_3$ P-H coupling) of **2a**



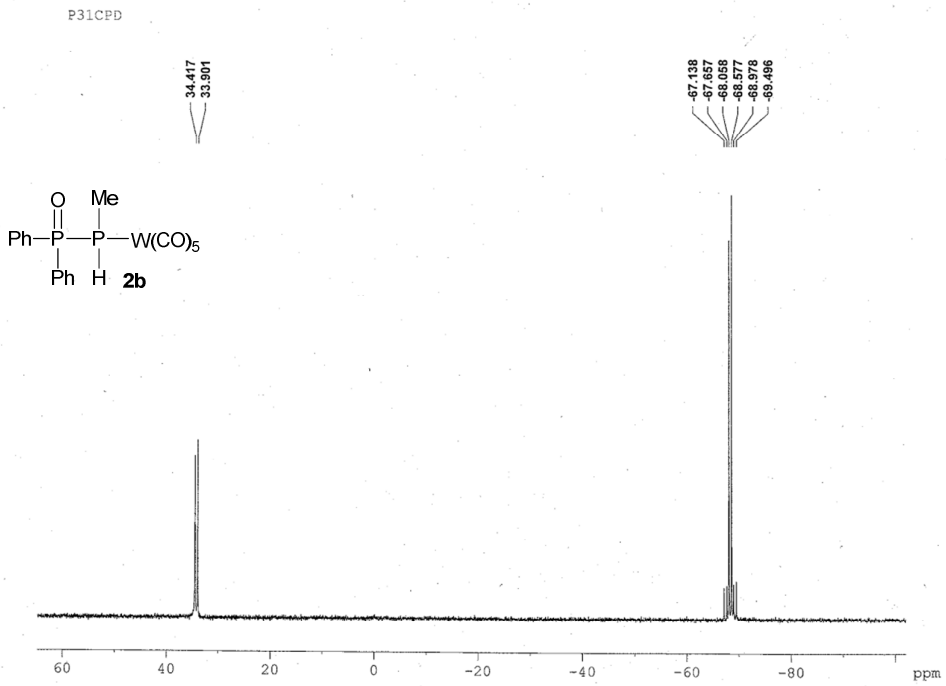
^{1}H NMR ($CDCl_3$) of **2a**



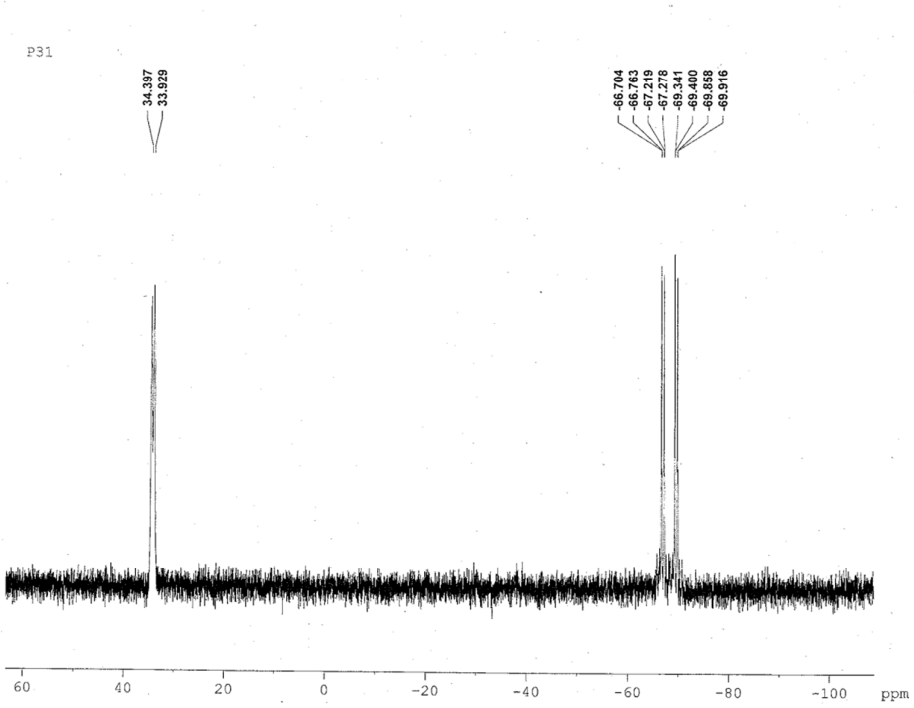
^{13}C NMR ($CDCl_3$) of **2a**



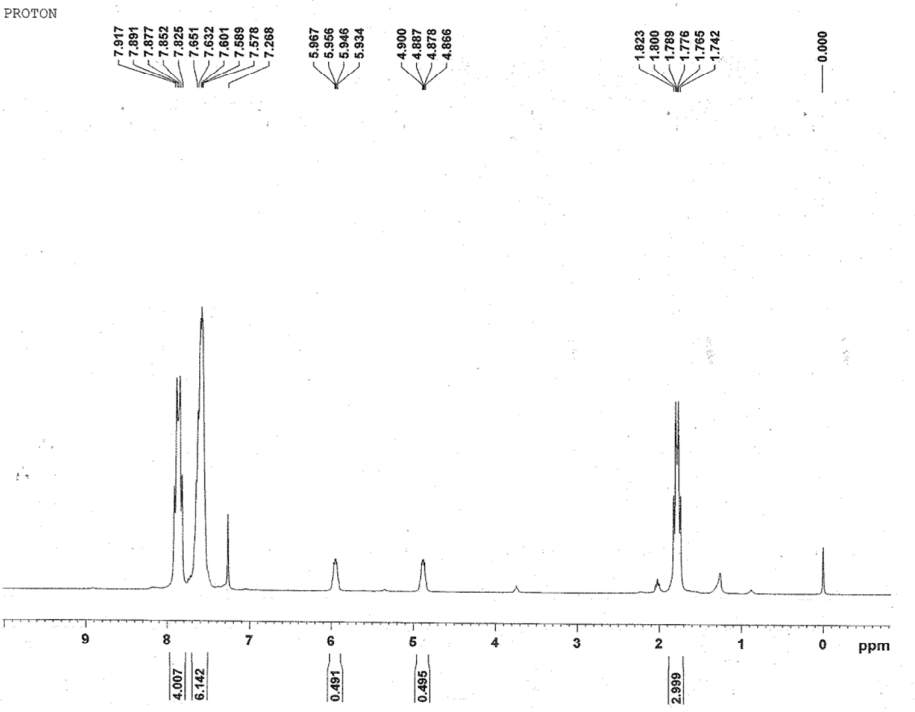
^{13}C NMR ($CDCl_3$) of **2a**



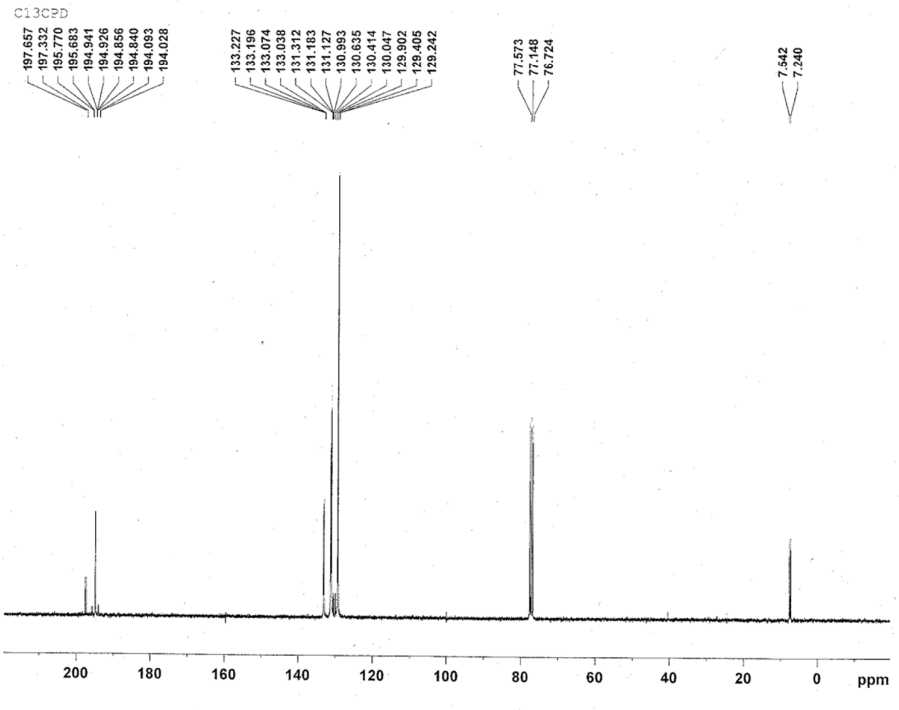
^{31}P CPD NMR ($CDCl_3$) of **2b**



^{31}P NMR ($CDCl_3$ P-H coupling) of **2b**



^{1}H NMR ($CDCl_3$) of **2b**



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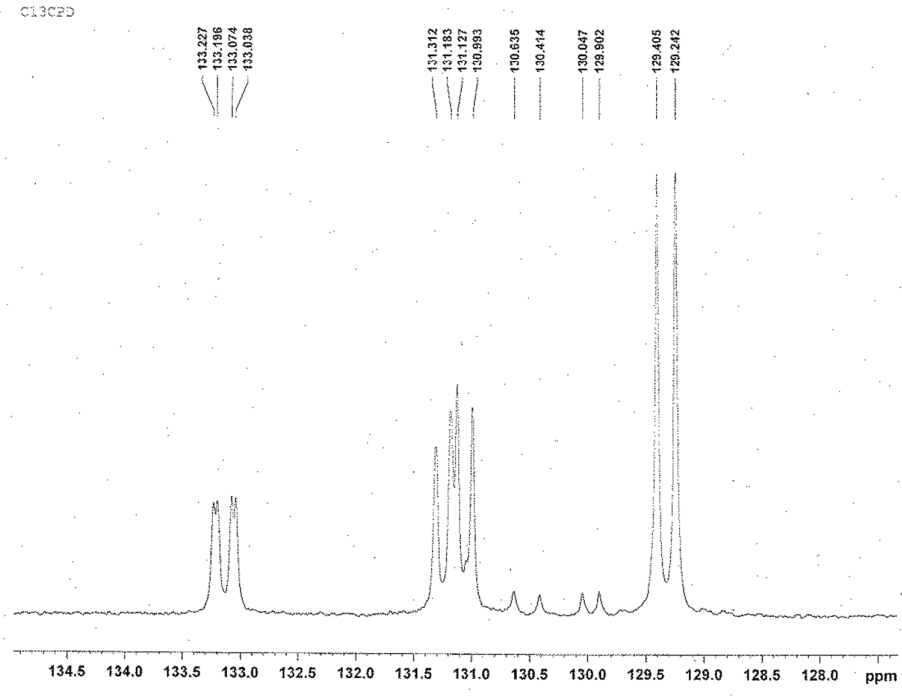
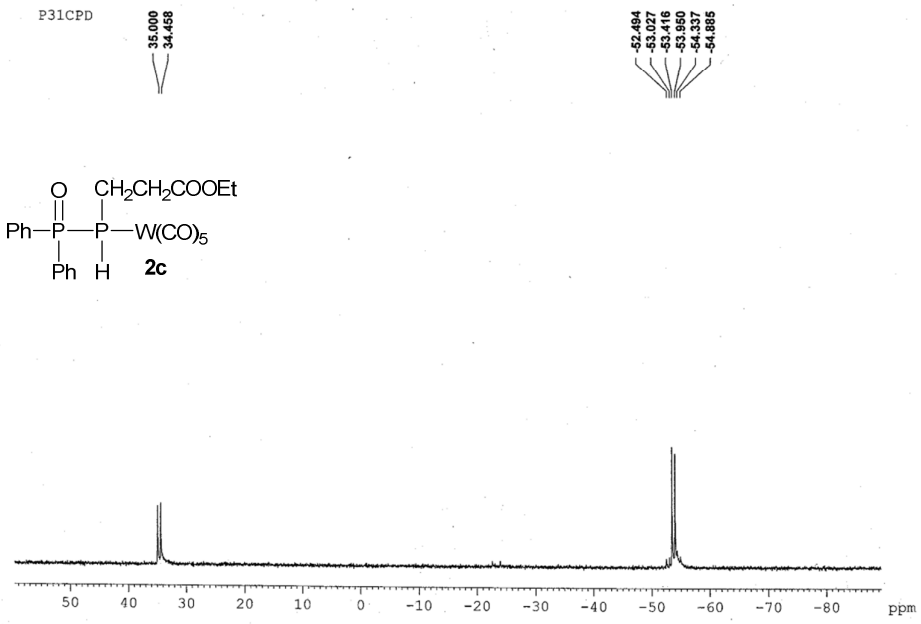
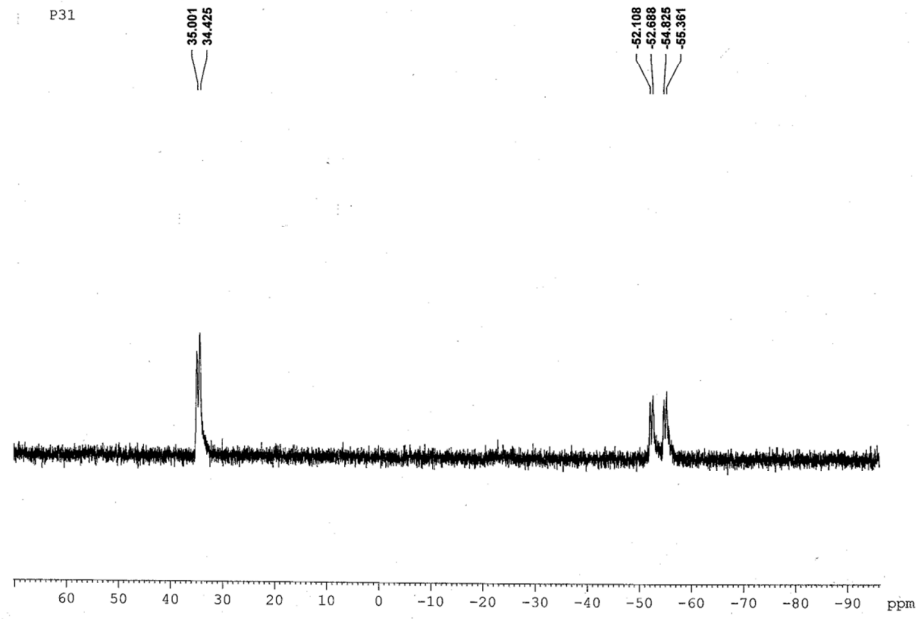


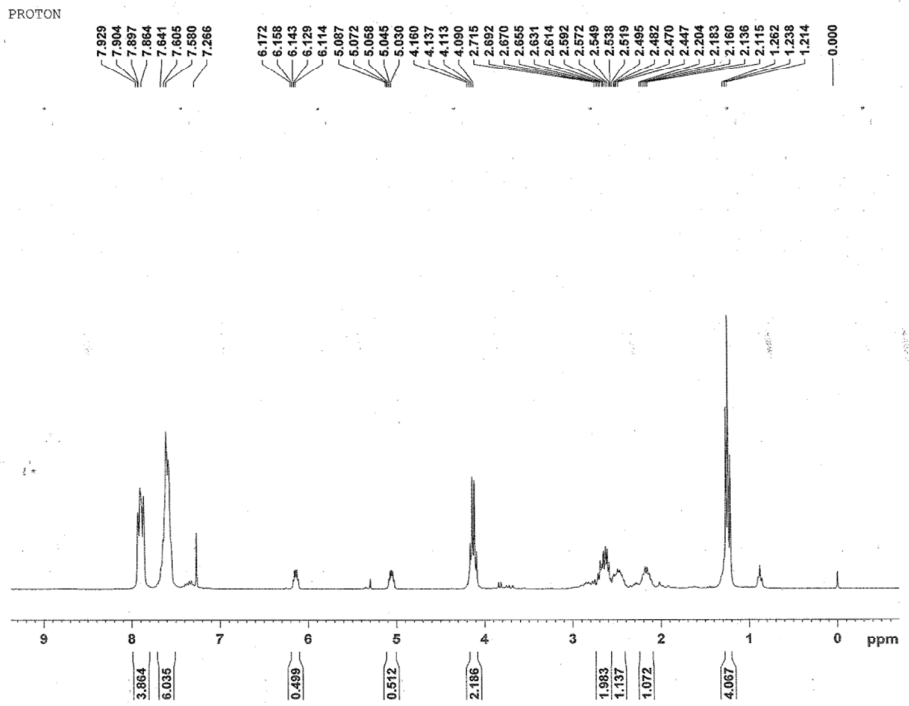
^{13}C NMR ($CDCl_3$) of **2b**



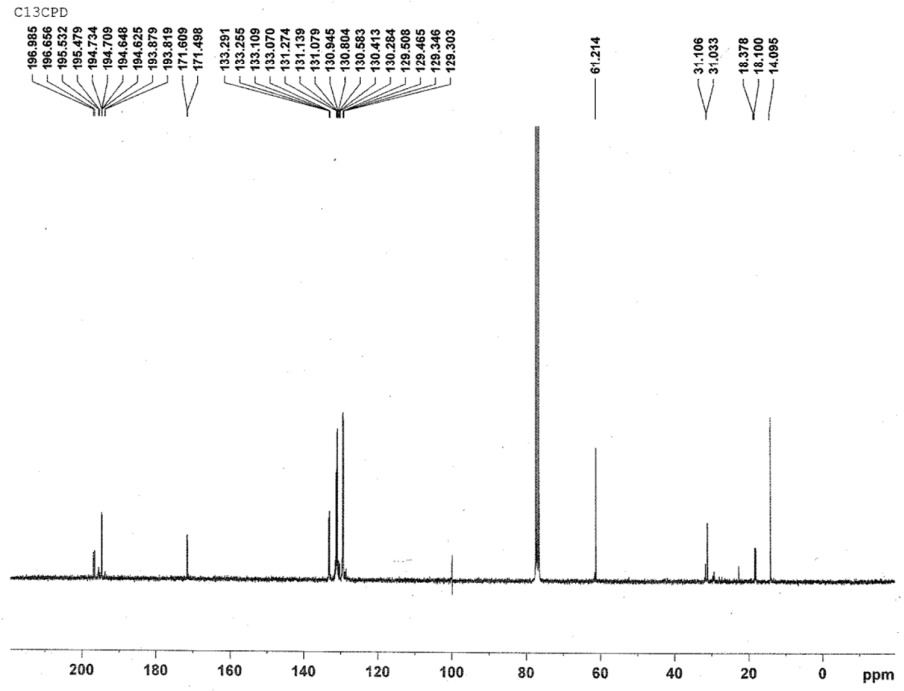
^{31}P CPD NMR ($CDCl_3$) of **2c**



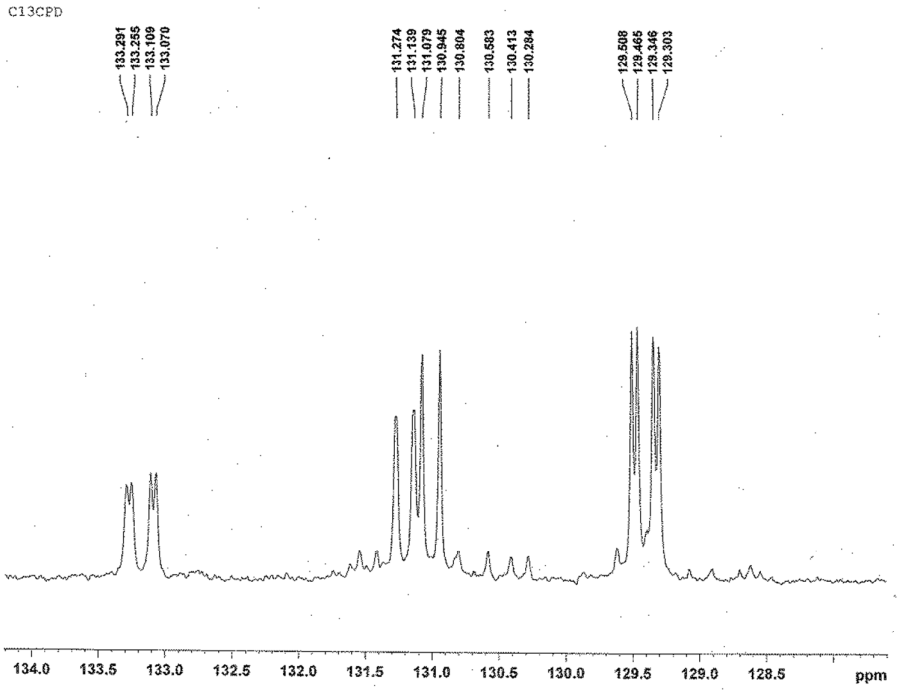
^{31}P NMR ($CDCl_3$ P-H coupling) of **2c**



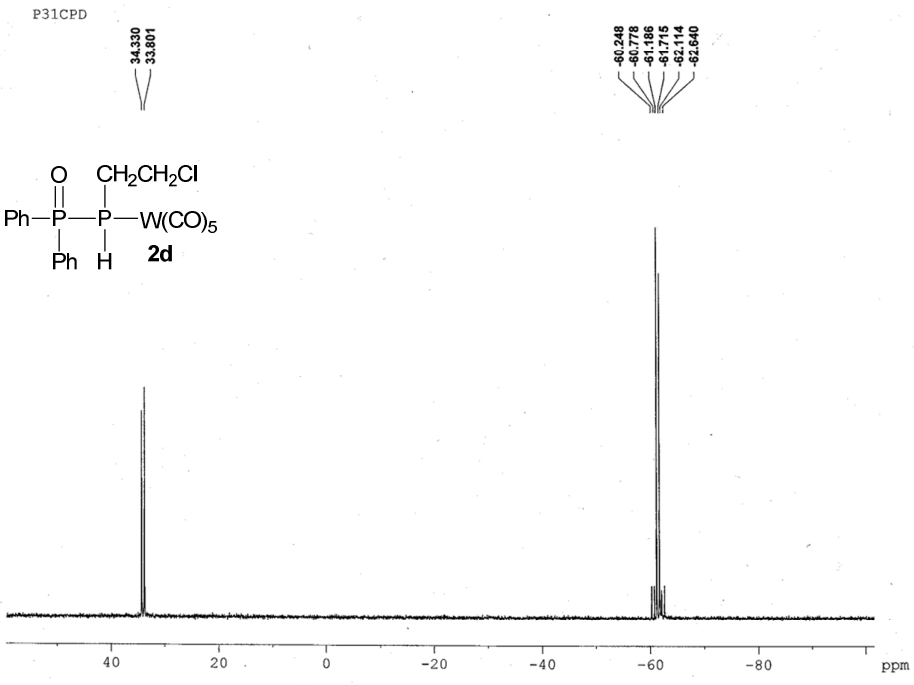
^{1}H NMR ($CDCl_3$) of **2c**



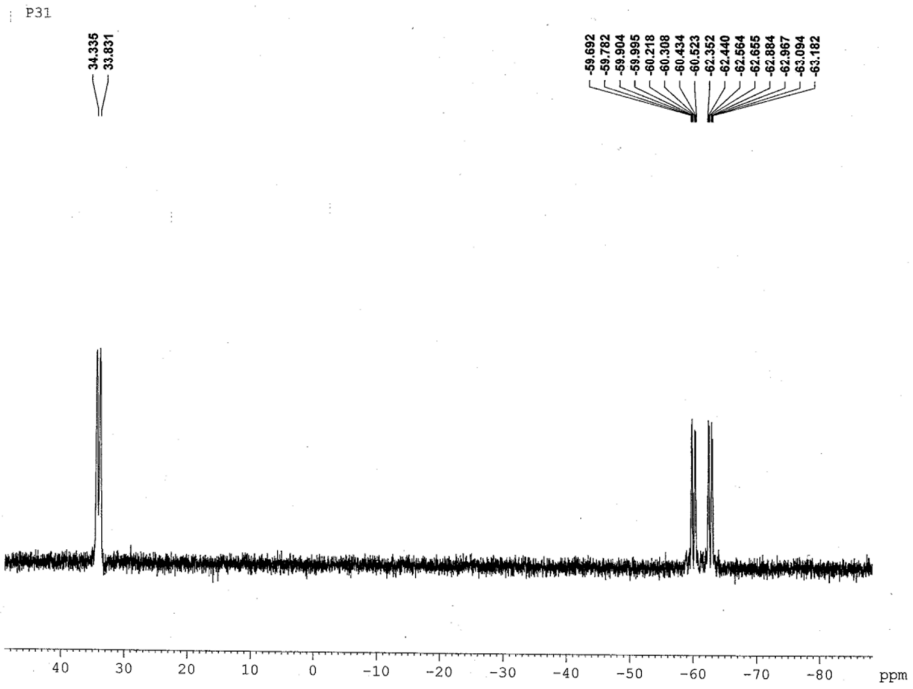
^{13}C NMR ($CDCl_3$) of **2c**



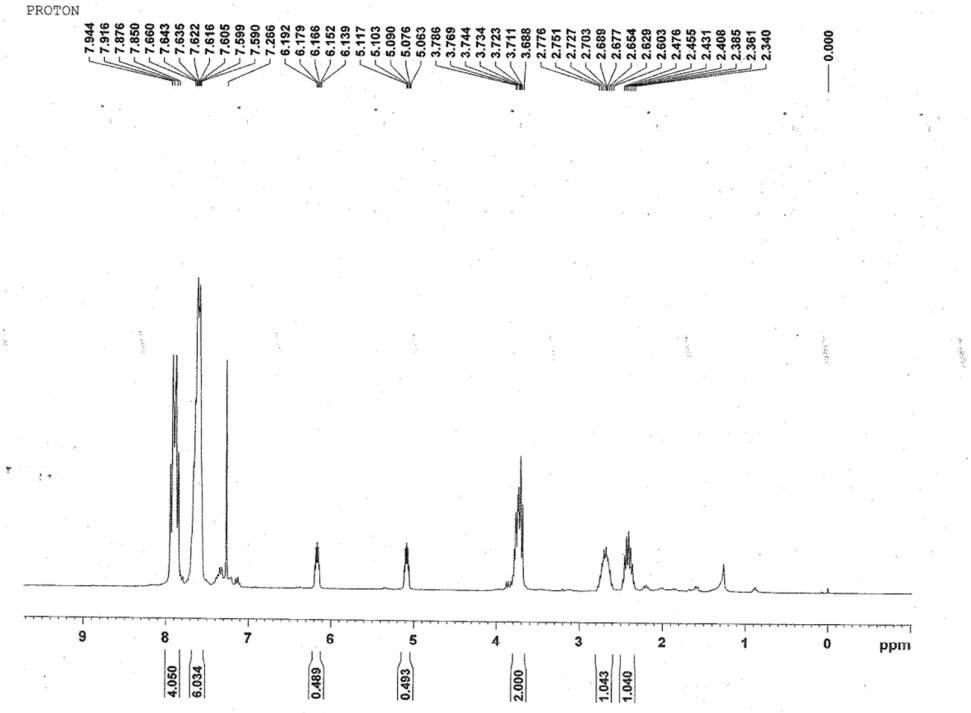
^{13}C NMR ($CDCl_3$) of **2c**



^{31}P CPD NMR ($CDCl_3$) of **2d**



^{31}P NMR ($CDCl_3$ P-H coupling) of **2d**



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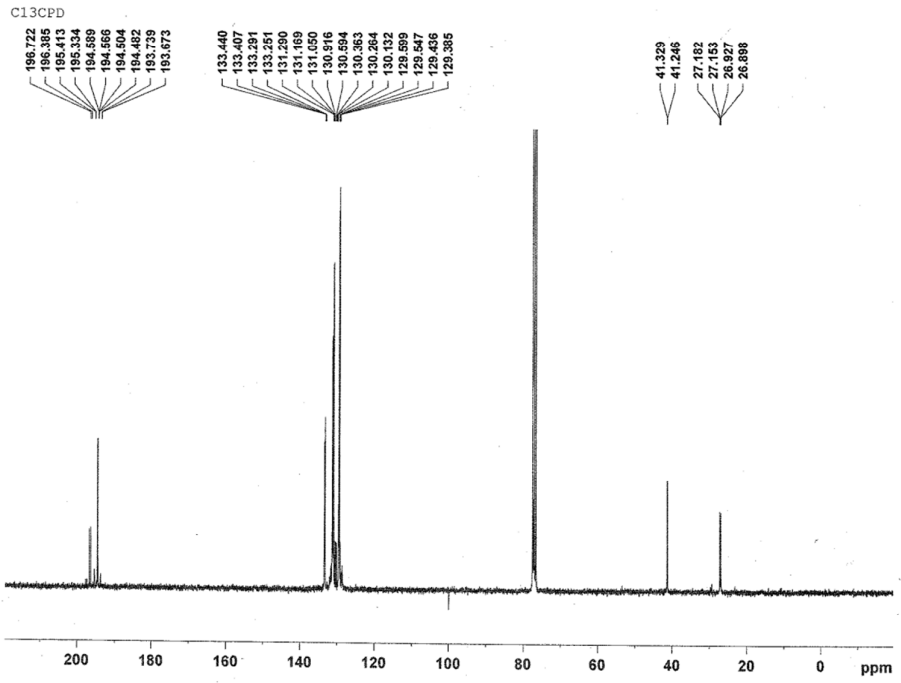

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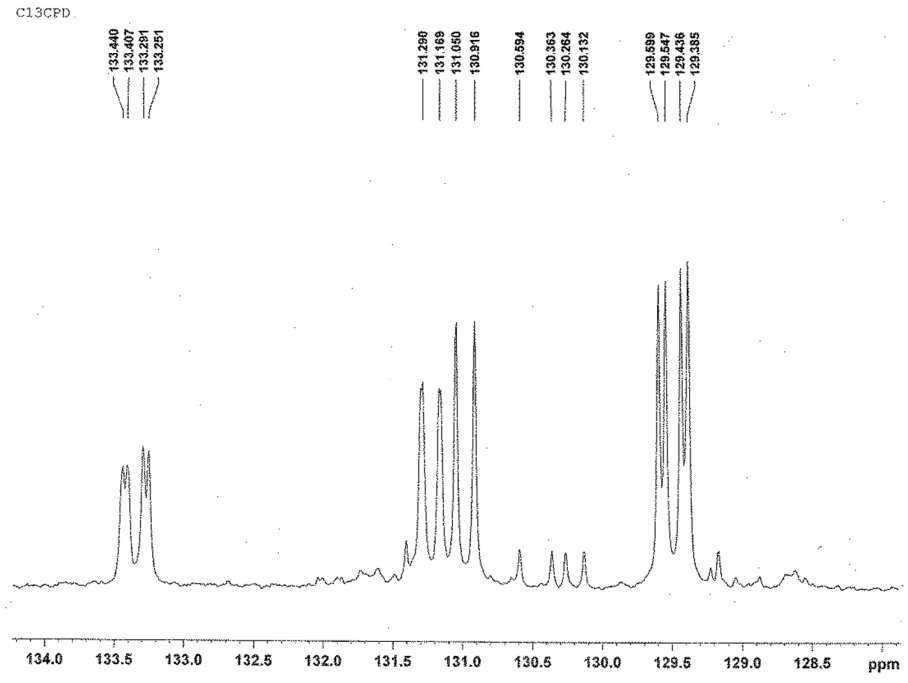

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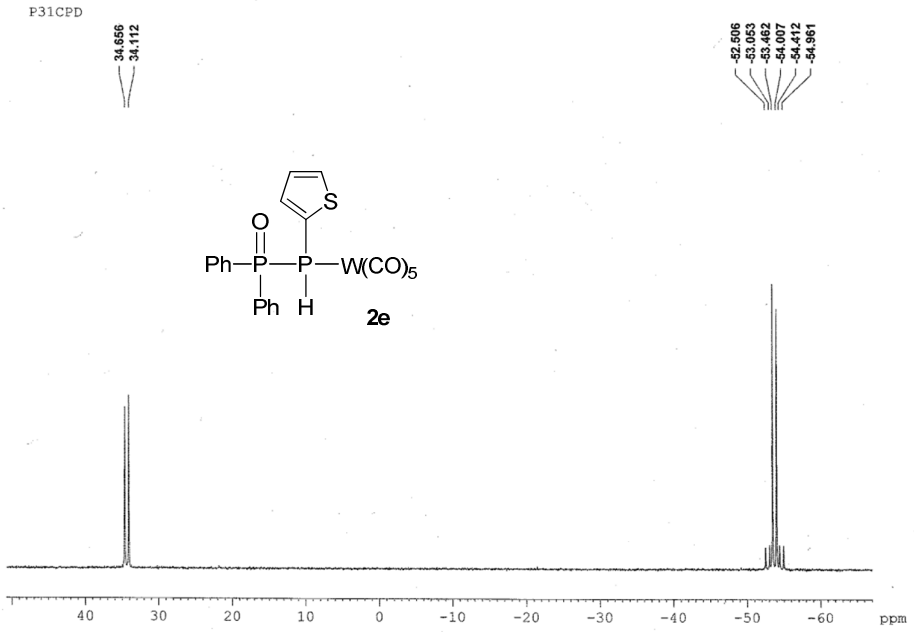
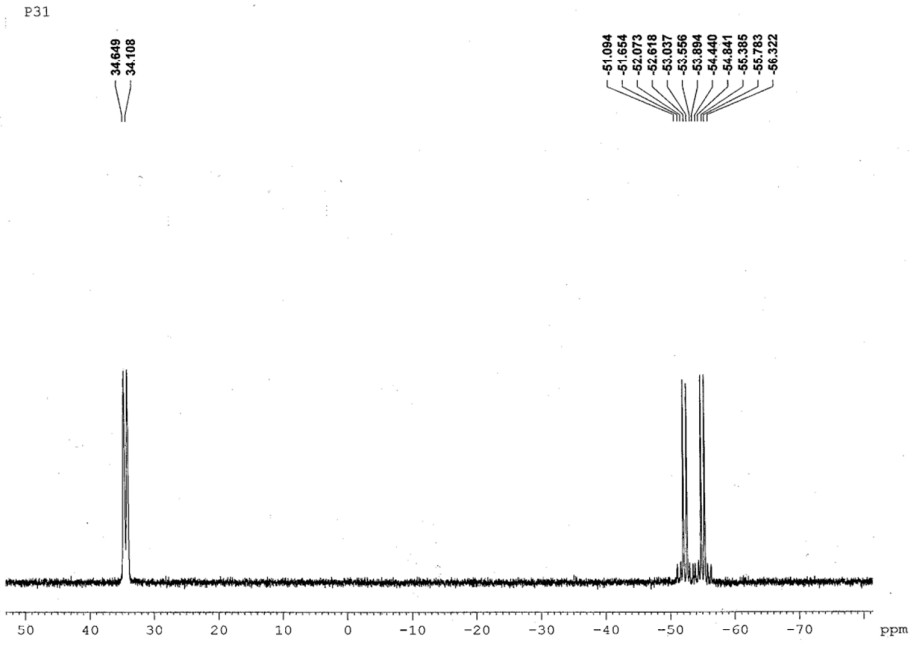
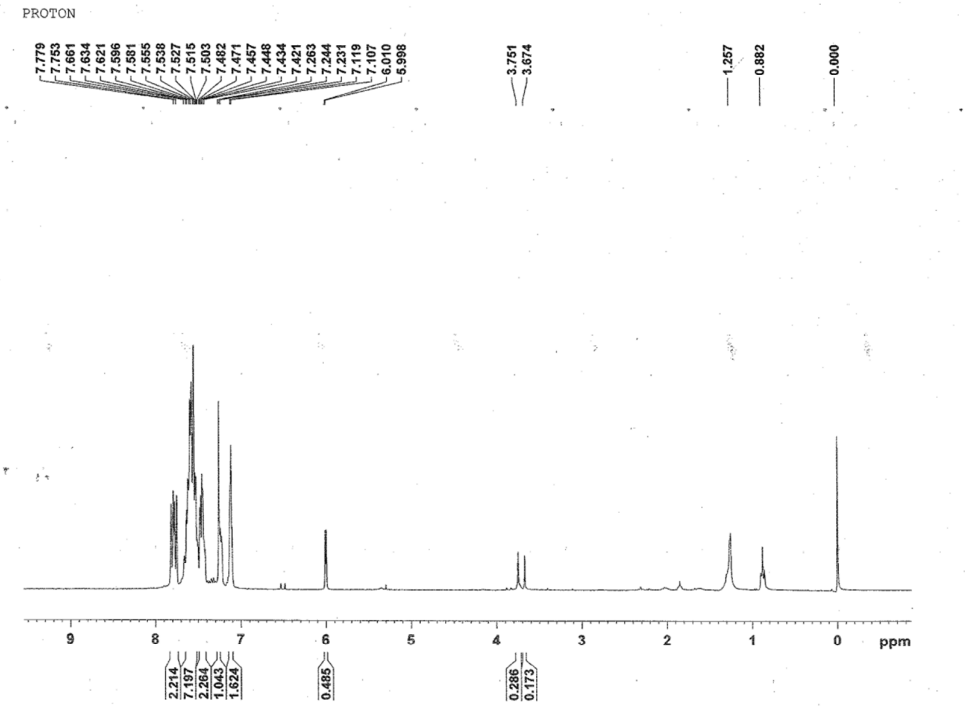


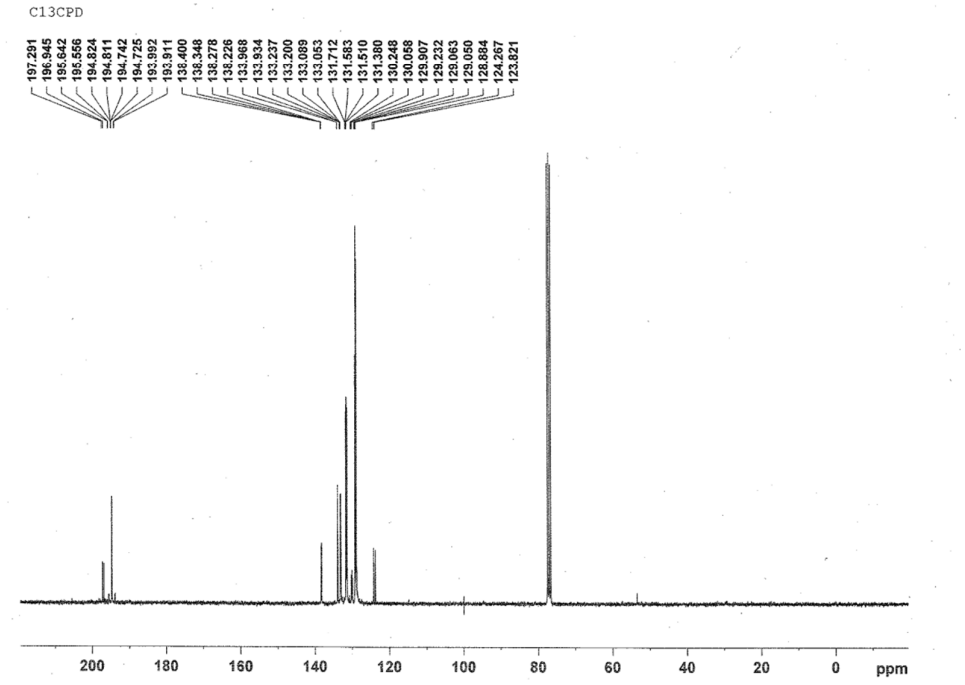
^{31}P CPD NMR ($CDCl_3$) of **2e**



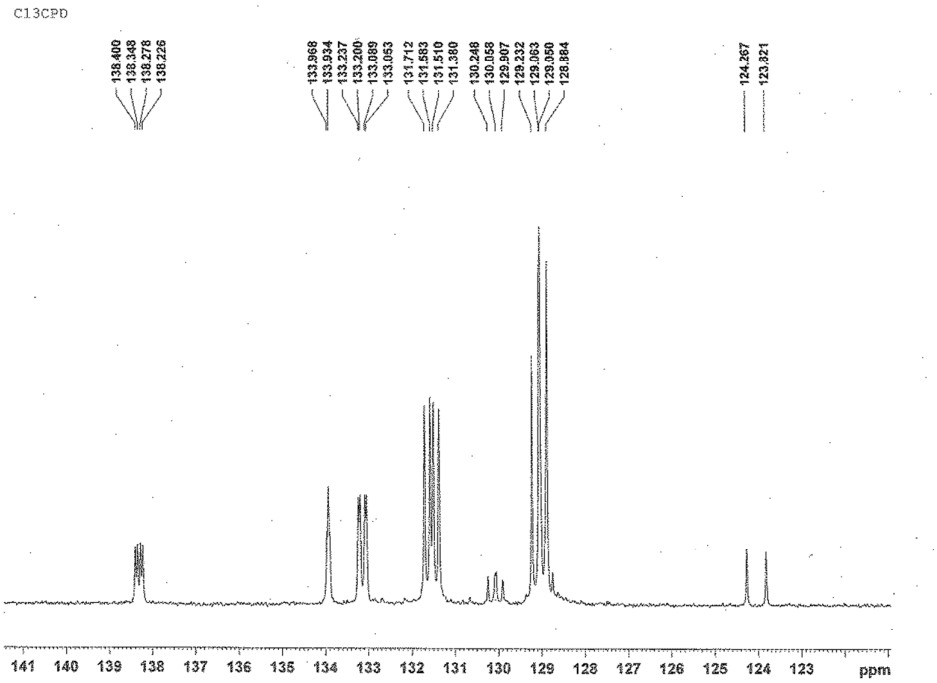
^{31}P NMR ($CDCl_3$ P-H coupling) of **2e**



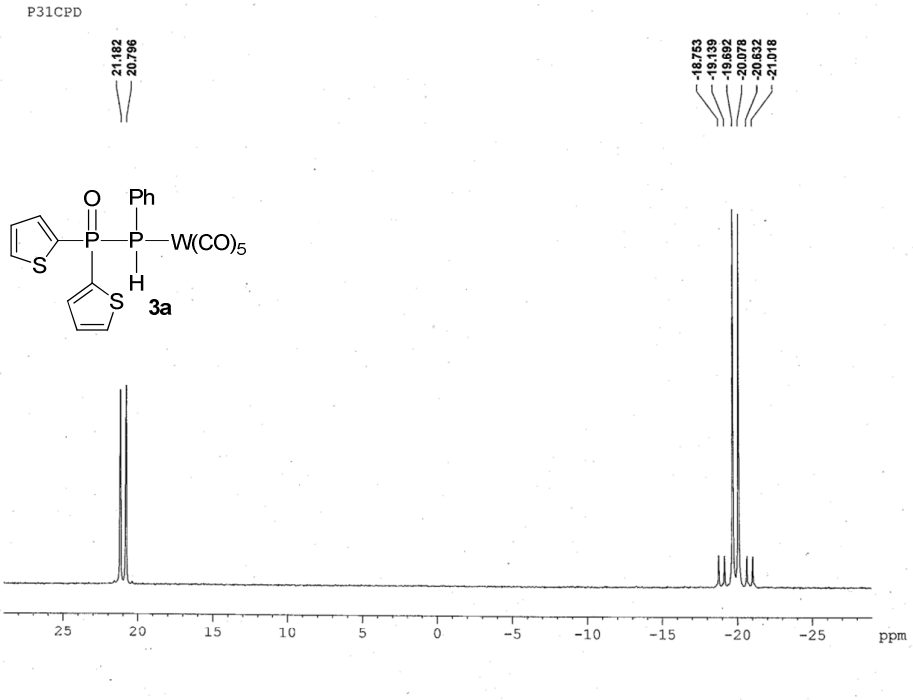
^{1}H NMR ($CDCl_3$) of **2e**



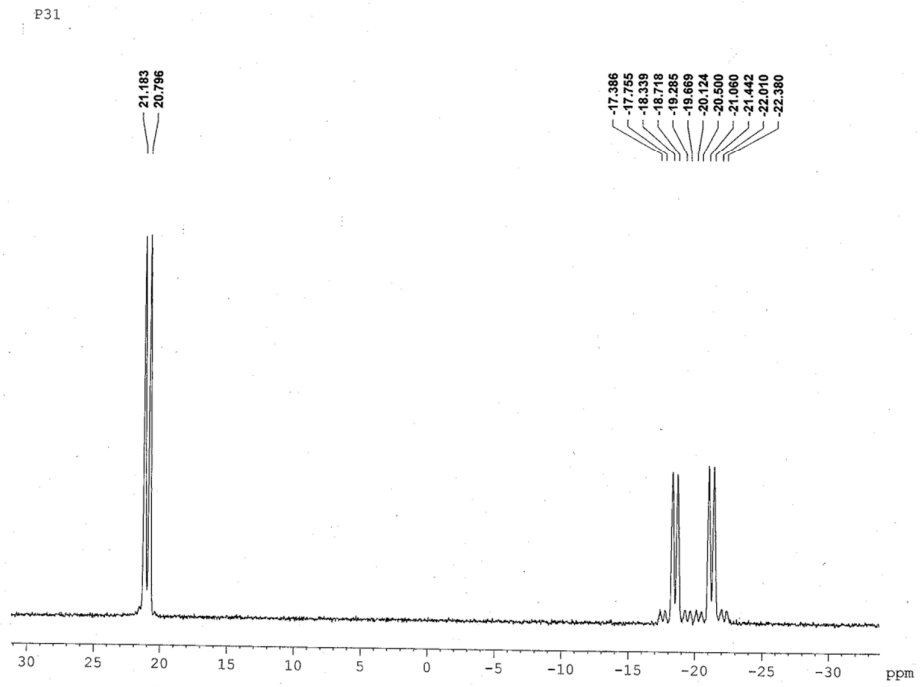
^{13}C NMR ($CDCl_3$) of **2e**



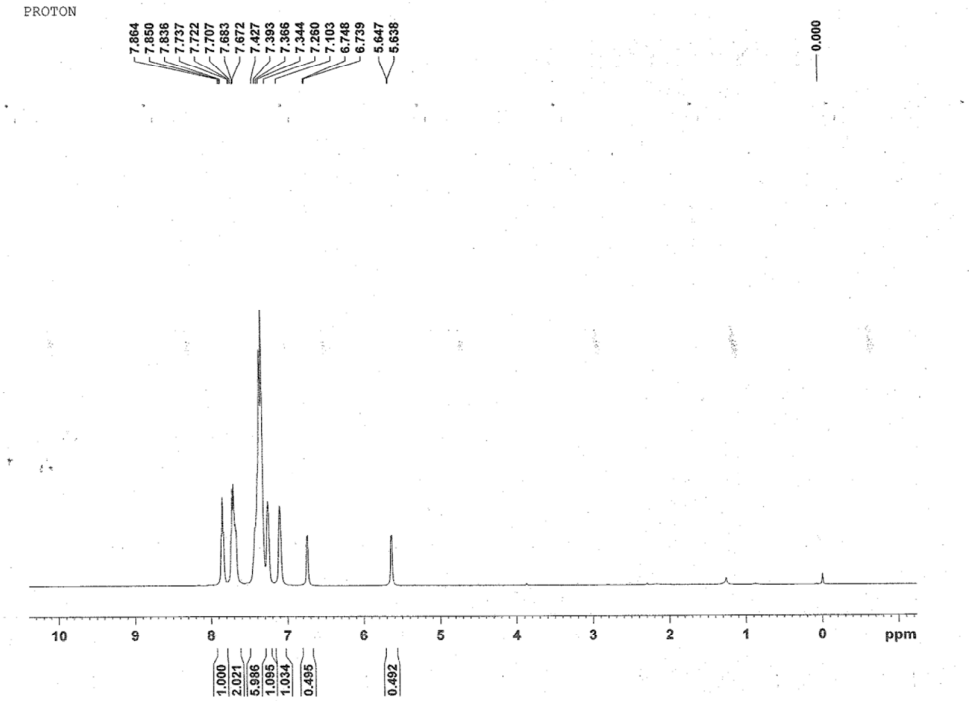
^{13}C NMR ($CDCl_3$) of **2e**



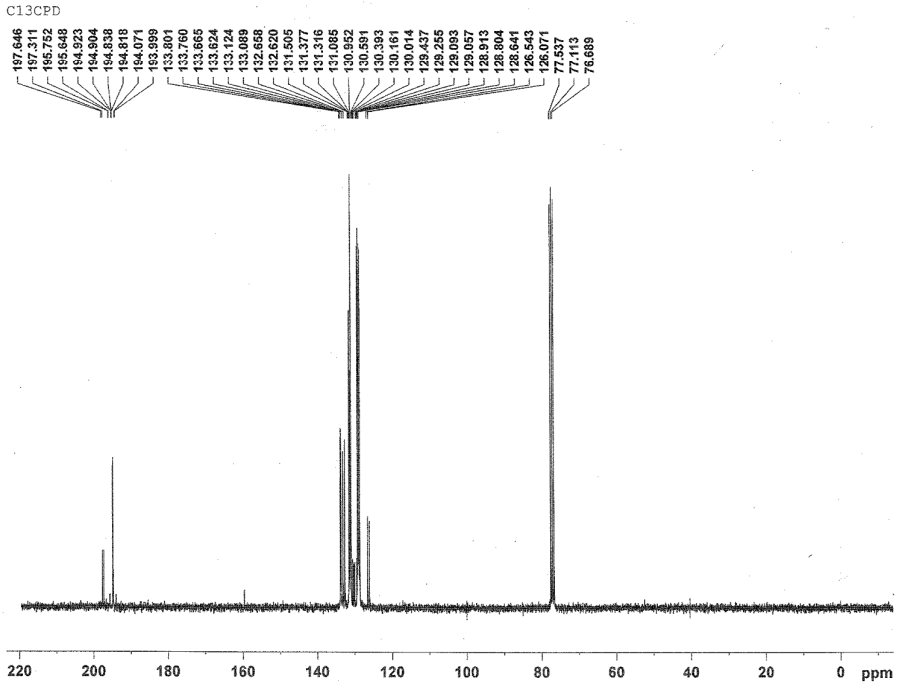
^{31}P CPD NMR ($CDCl_3$) of **2f**



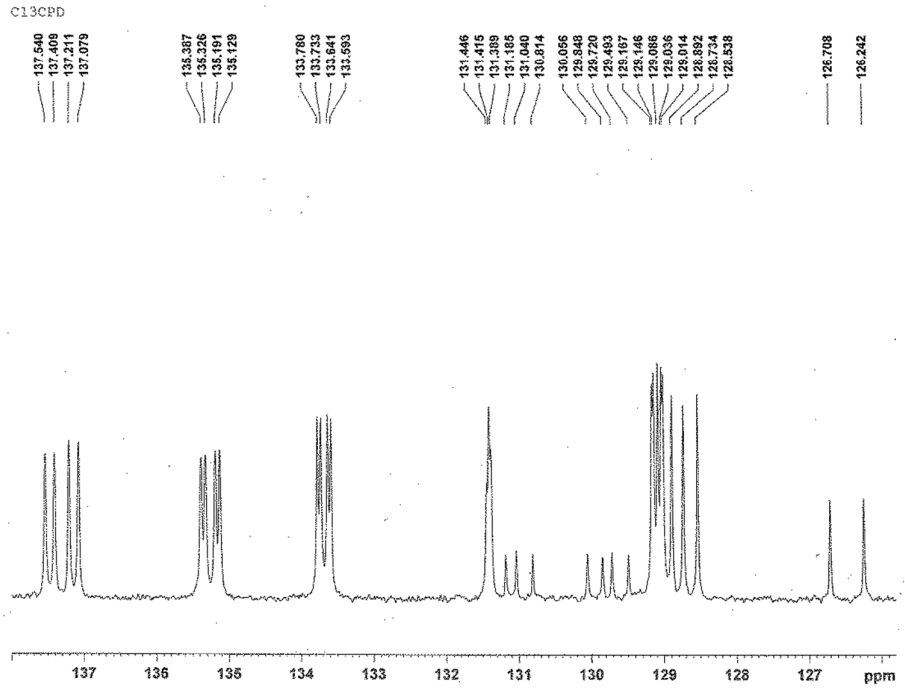
^{31}P NMR ($CDCl_3$ P-H coupling) of **2f**



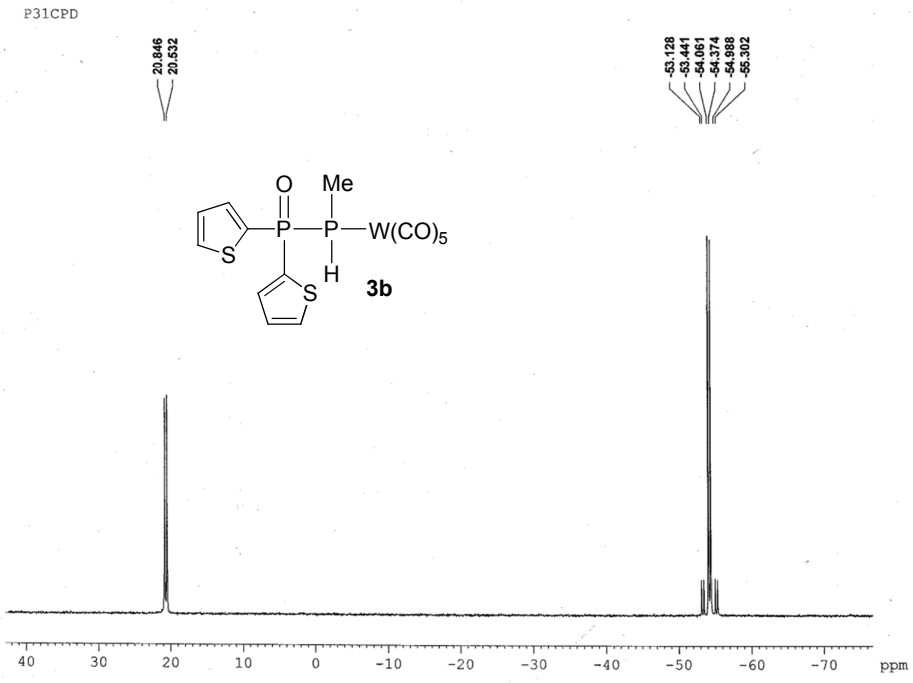
^{1}H NMR ($CDCl_3$) of **2f**



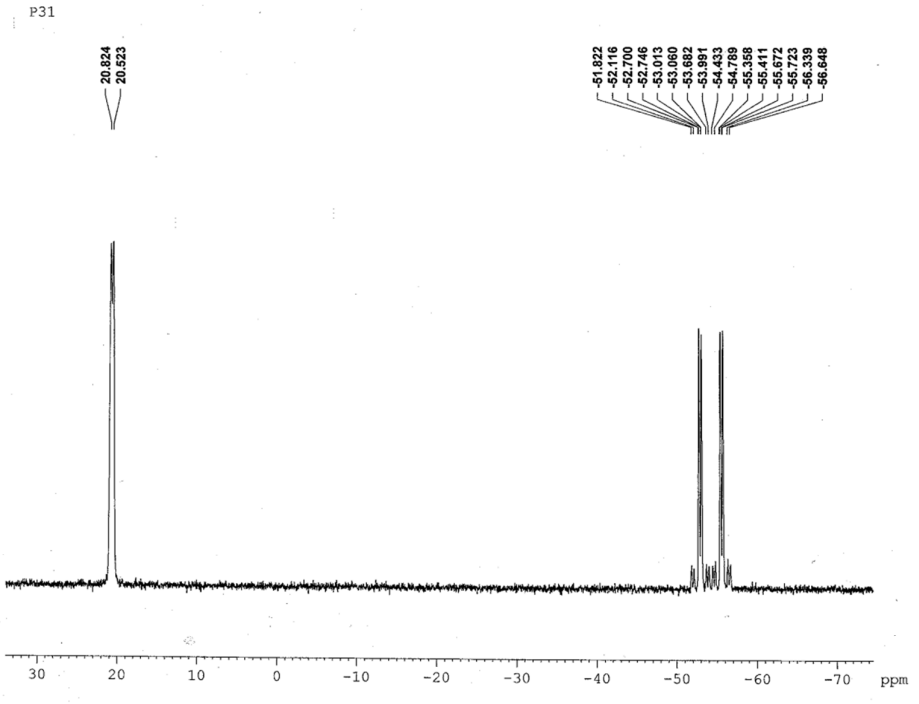
^{13}C NMR ($CDCl_3$) of **2f**



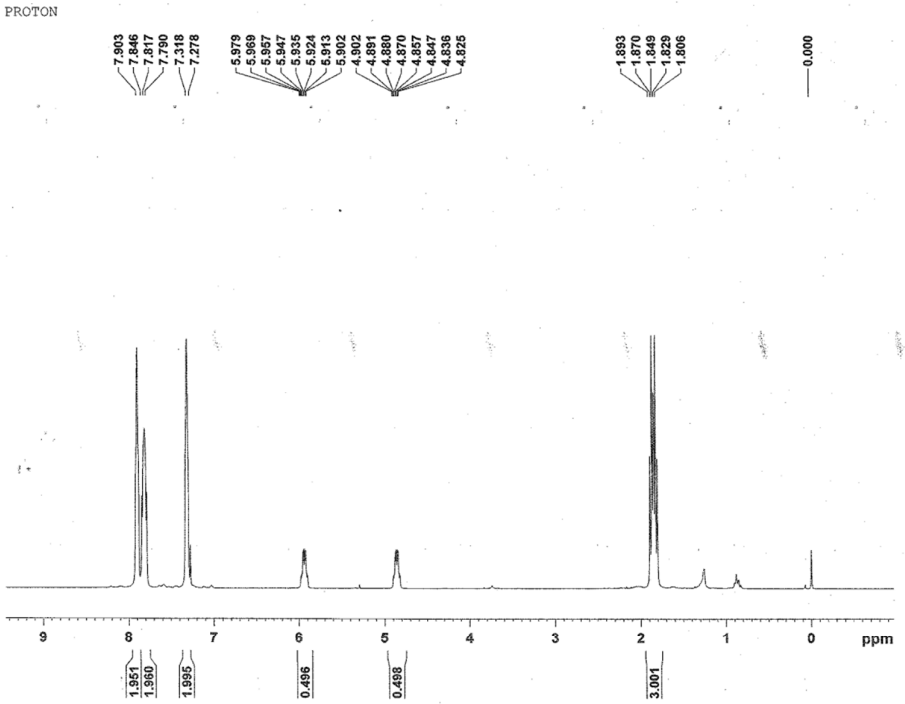
^{13}C NMR ($CDCl_3$) of **2f**



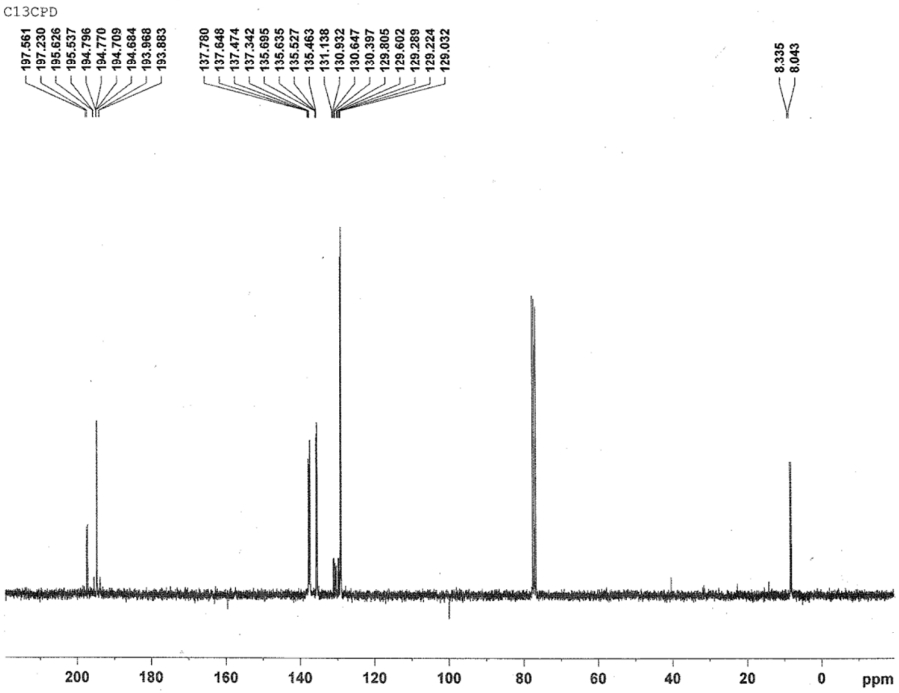
^{31}P CPD NMR ($CDCl_3$) of **2g**



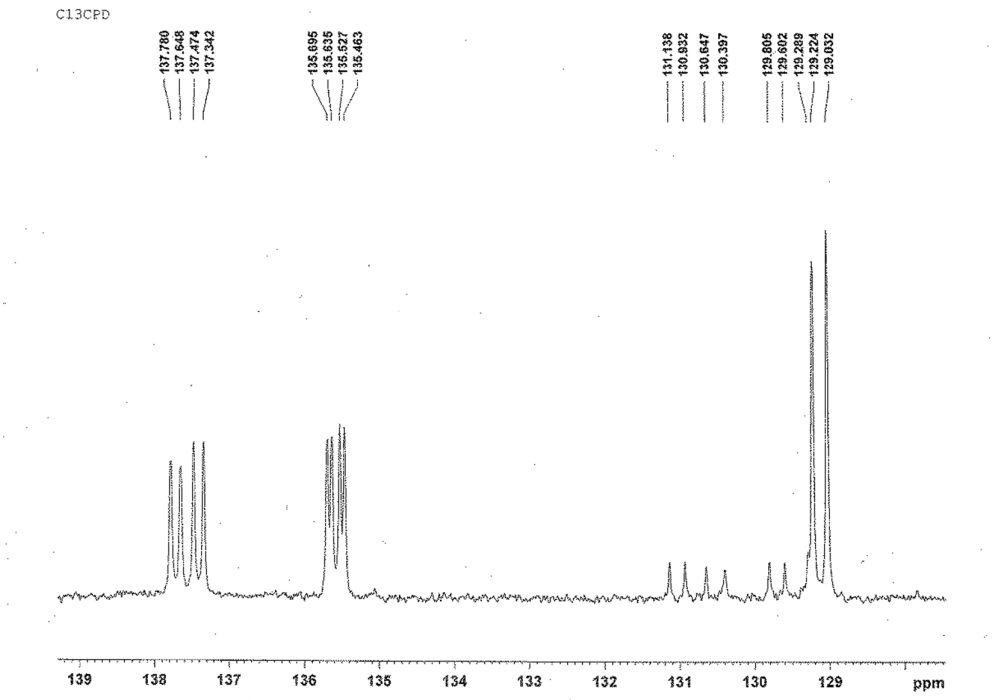
^{31}P NMR ($CDCl_3$ P-H coupling) of **2g**



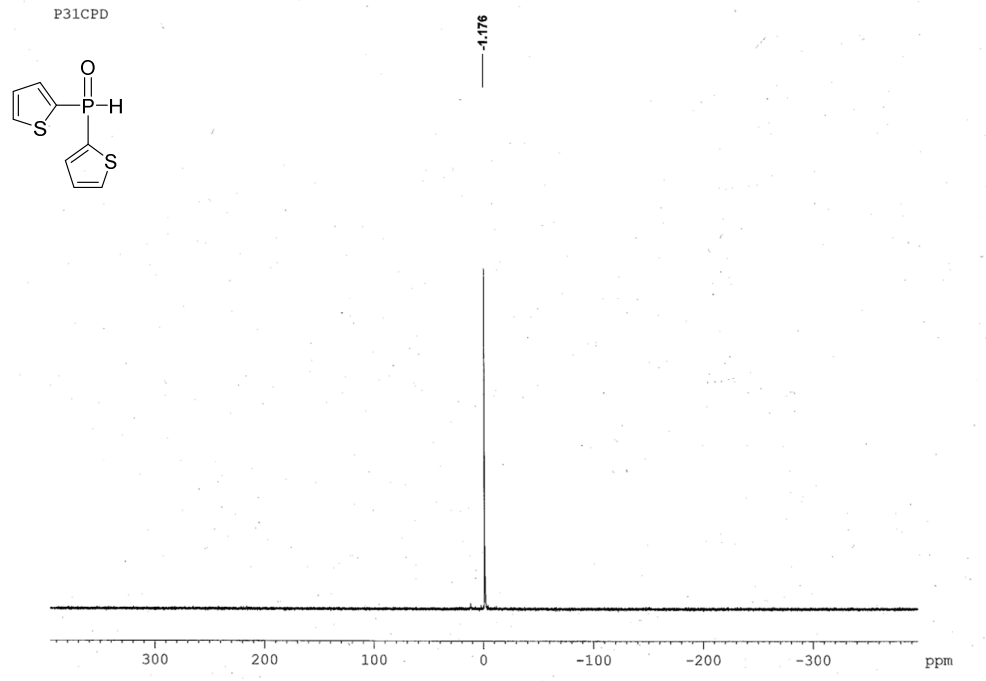
^{1}H NMR ($CDCl_3$) of **2g**



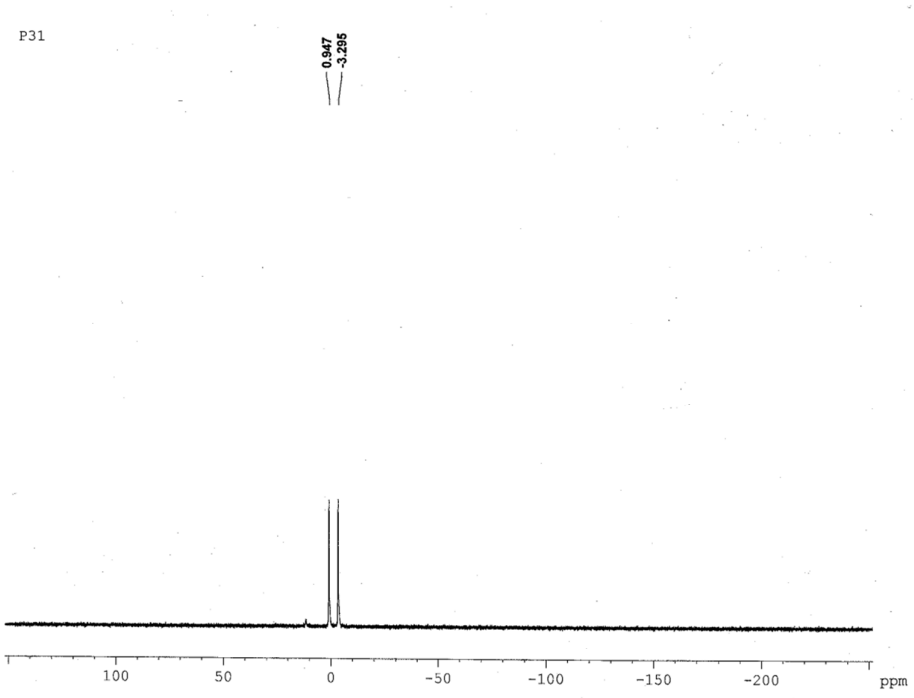
^{13}C NMR ($CDCl_3$) of **2g**



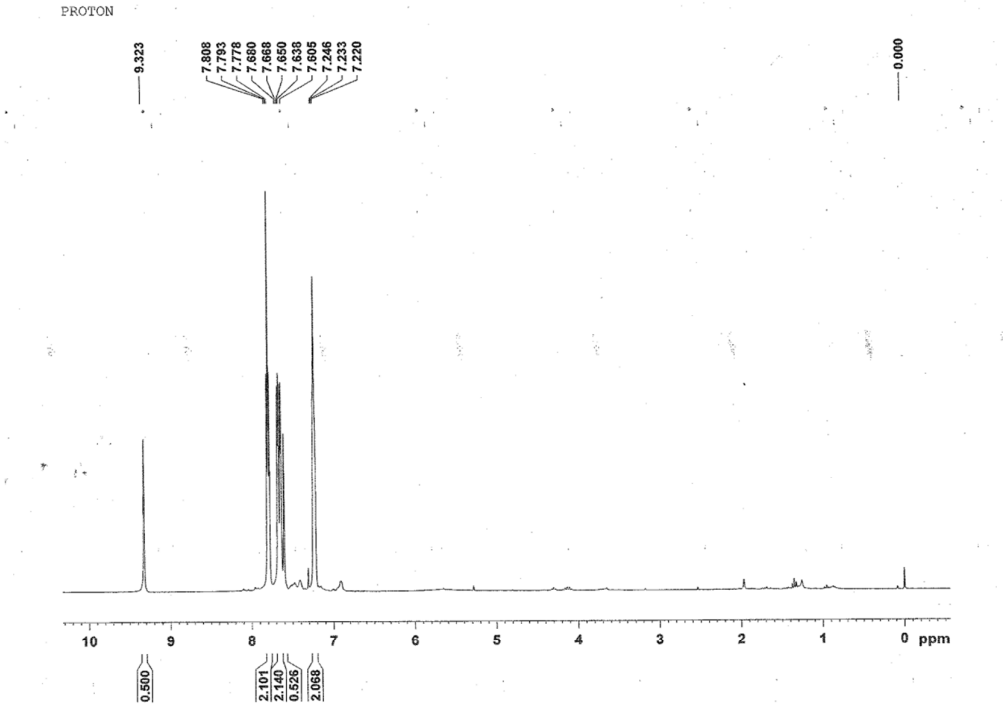
^{13}C NMR ($CDCl_3$) of **2g**



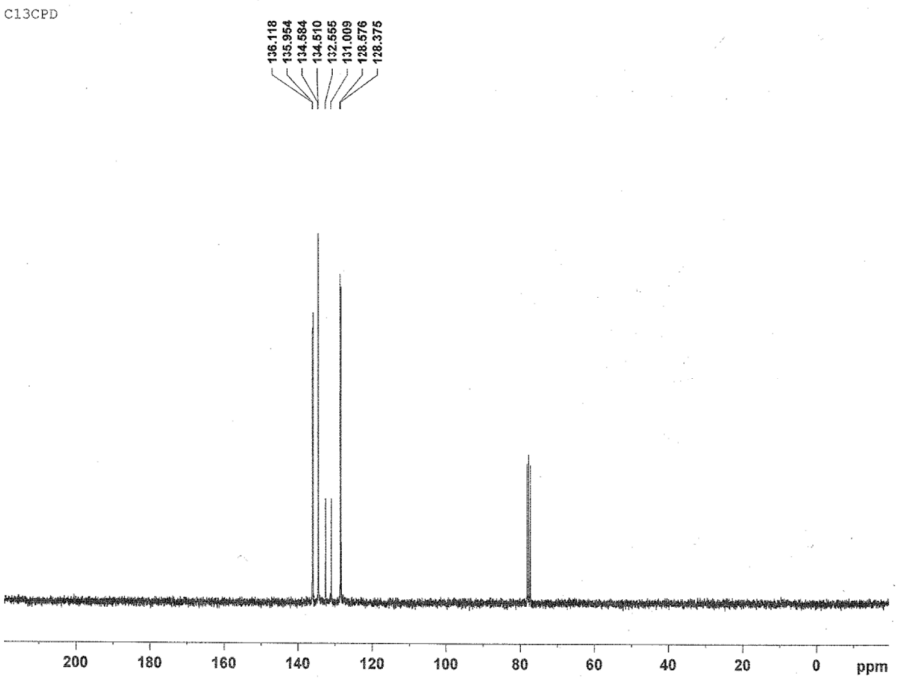
^{31}P CPD NMR ($CDCl_3$) of dithienylphosphine oxide



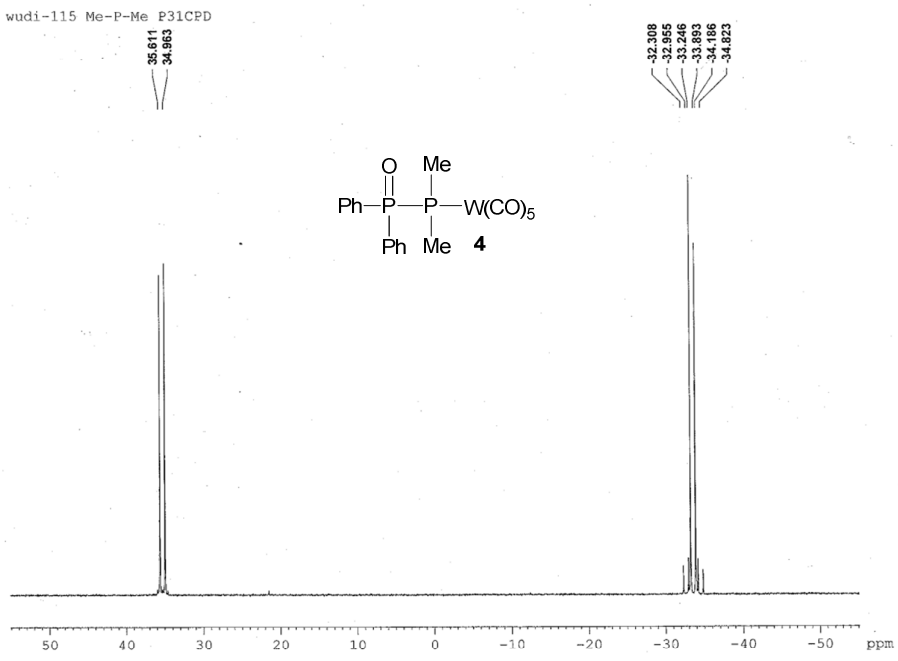
^{31}P NMR ($CDCl_3$ P-H coupling) of dithienylphosphine oxide



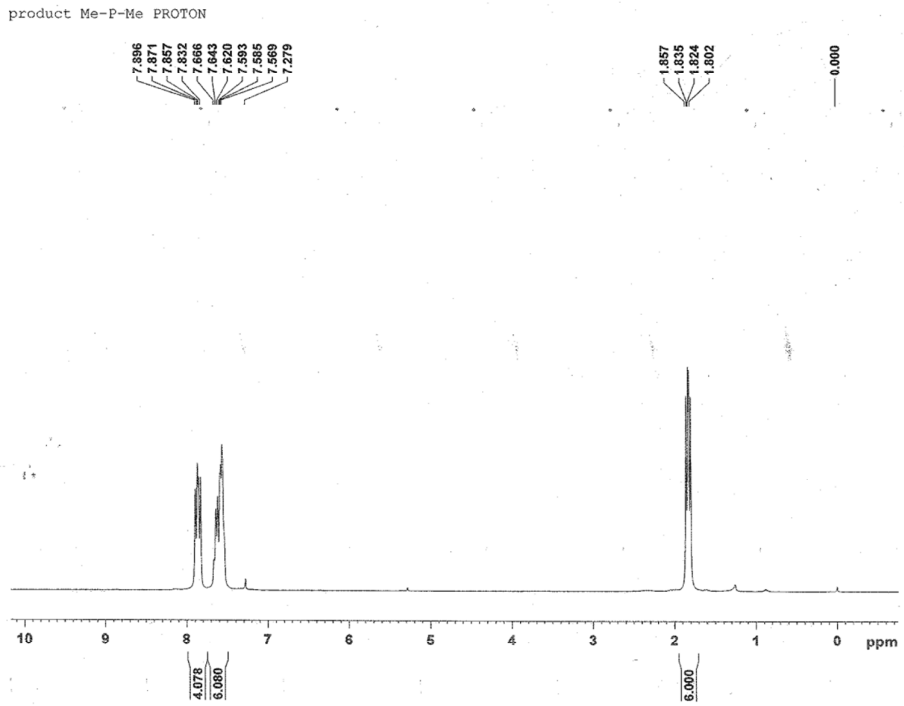
^{1}H NMR ($CDCl_3$) of dithienylphosphine oxide



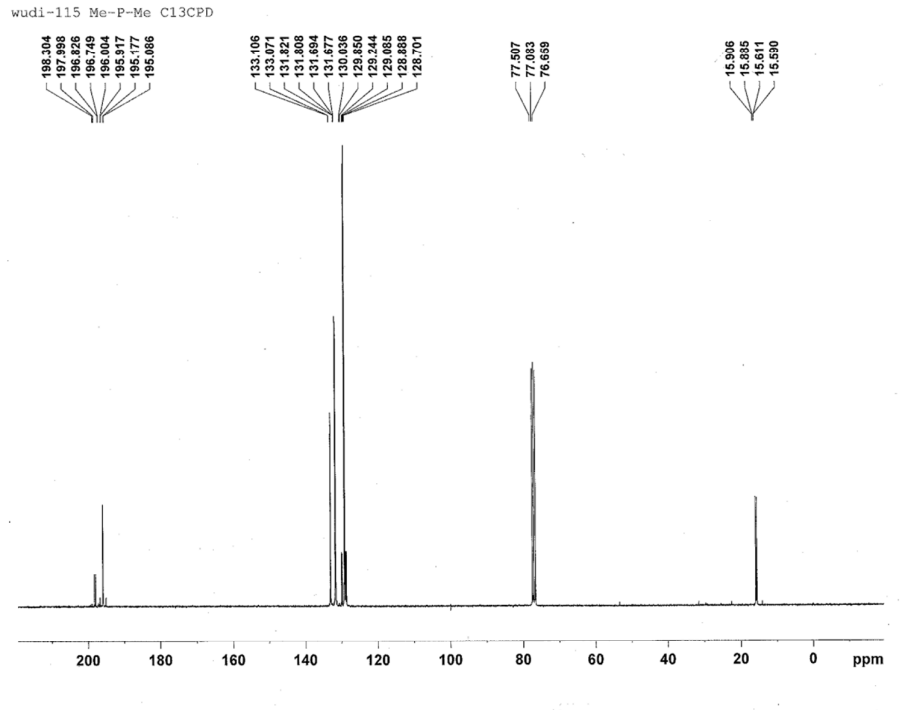
^{13}C NMR ($CDCl_3$) of dithienylphosphine oxide



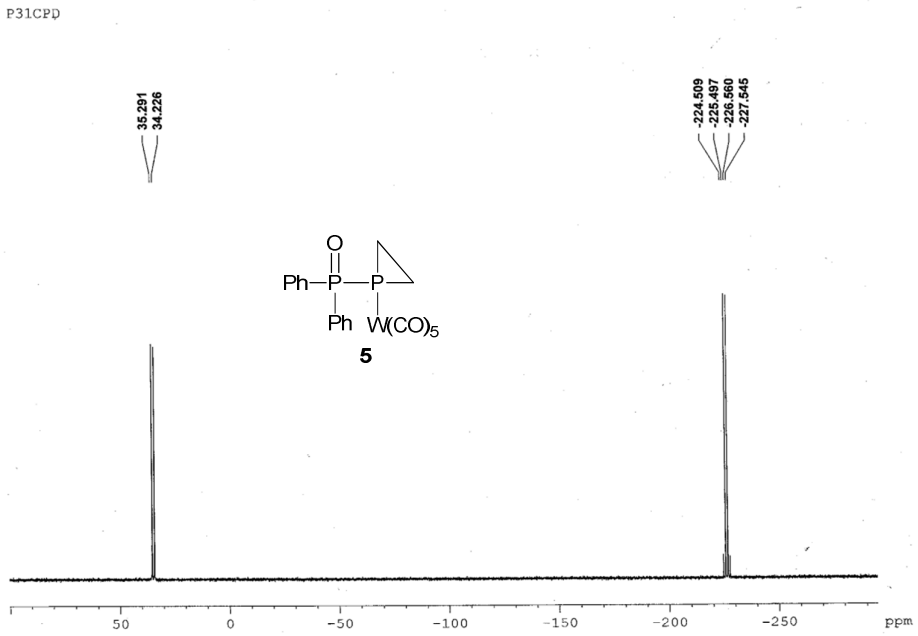
^{31}P CPD NMR ($CDCl_3$) of **4**



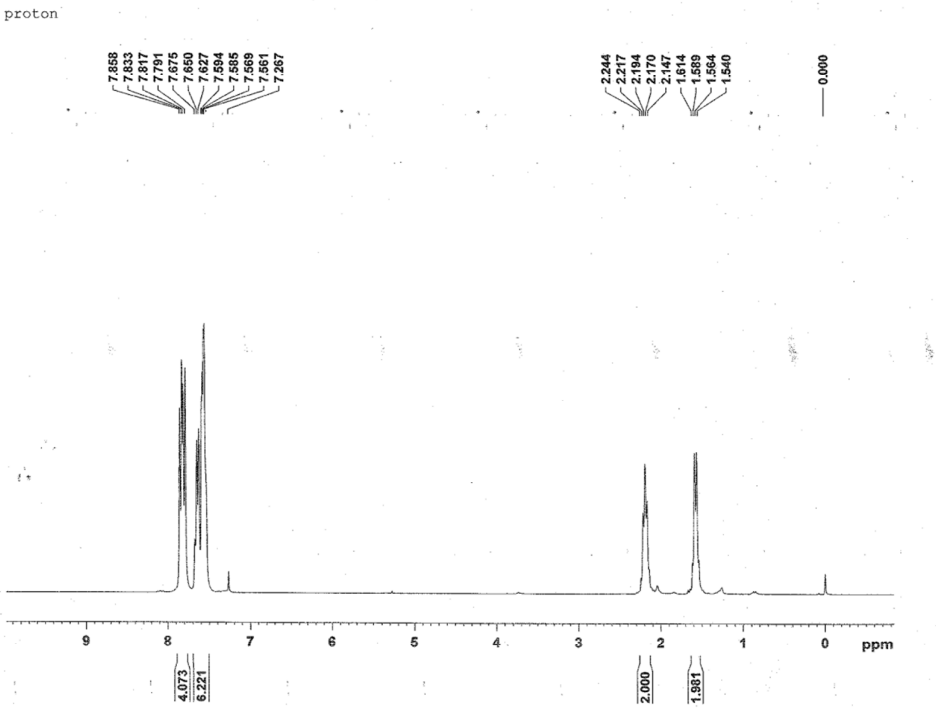
^{1}H NMR ($CDCl_3$) of **4**



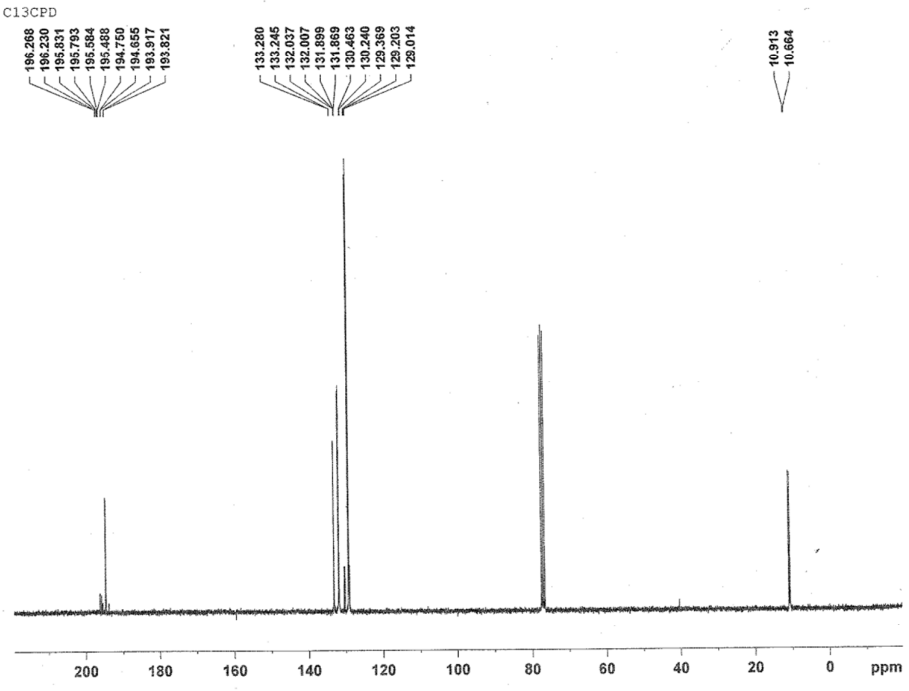
^{13}C NMR ($CDCl_3$) of **4**



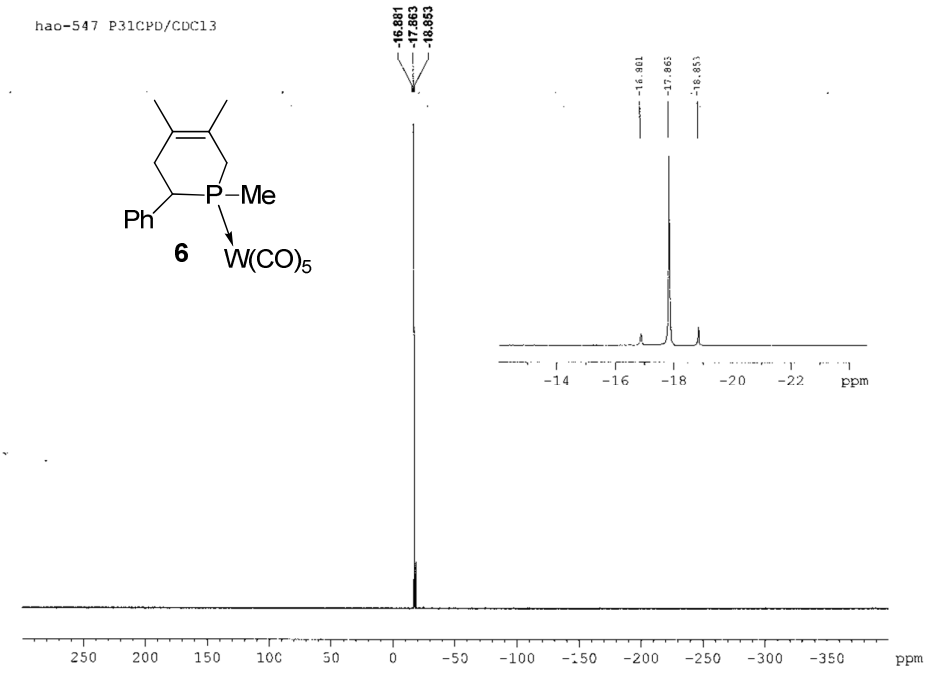
^{31}P CPD NMR ($CDCl_3$) of **5**



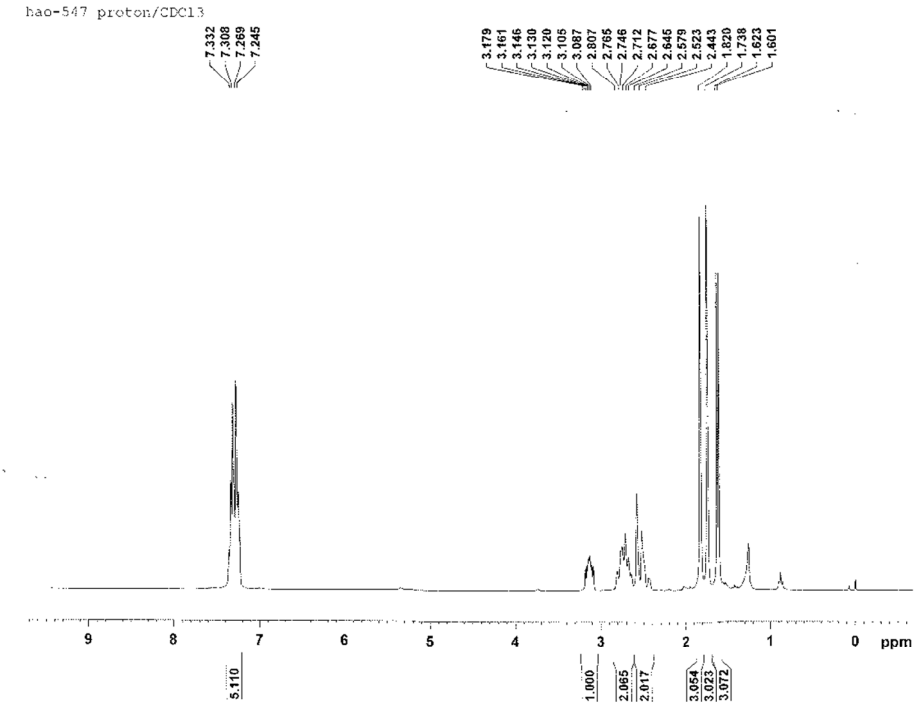
^{1}H NMR ($CDCl_3$) of **5**



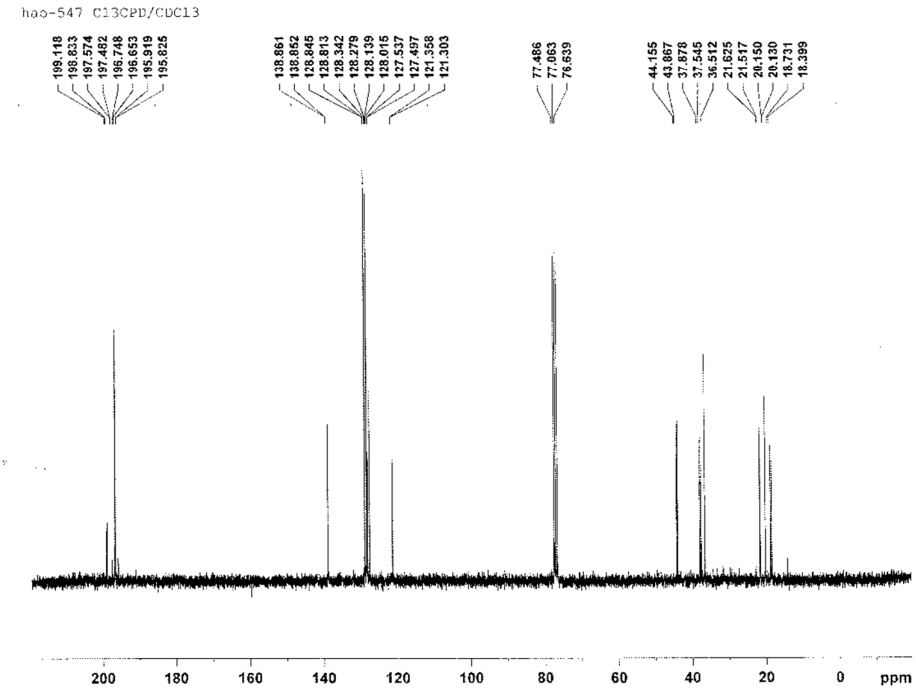
^{13}C NMR ($CDCl_3$) of **5**



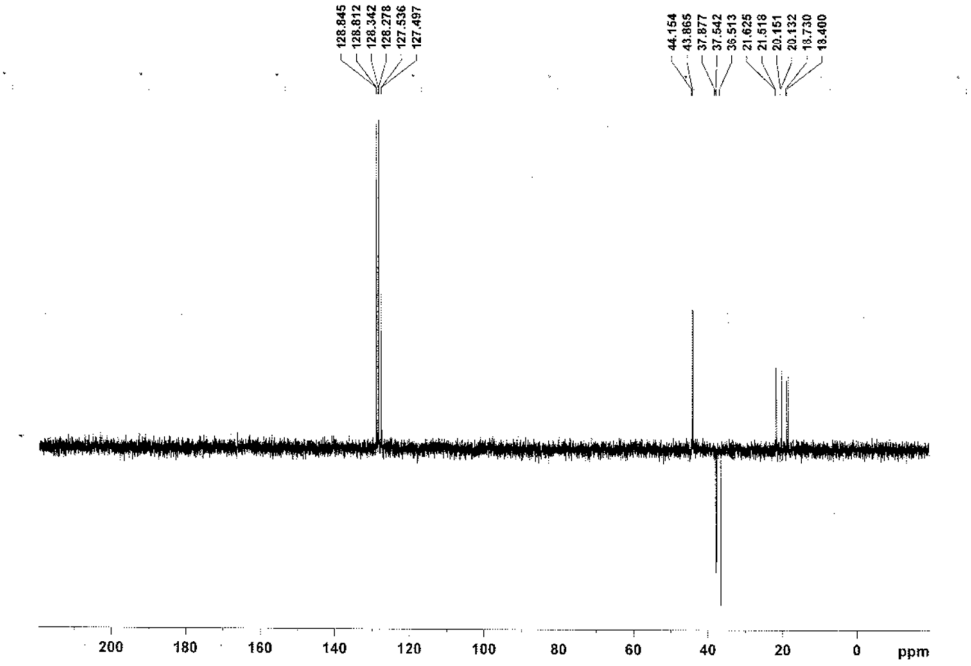
^{31}P CPD NMR ($CDCl_3$) of **6**



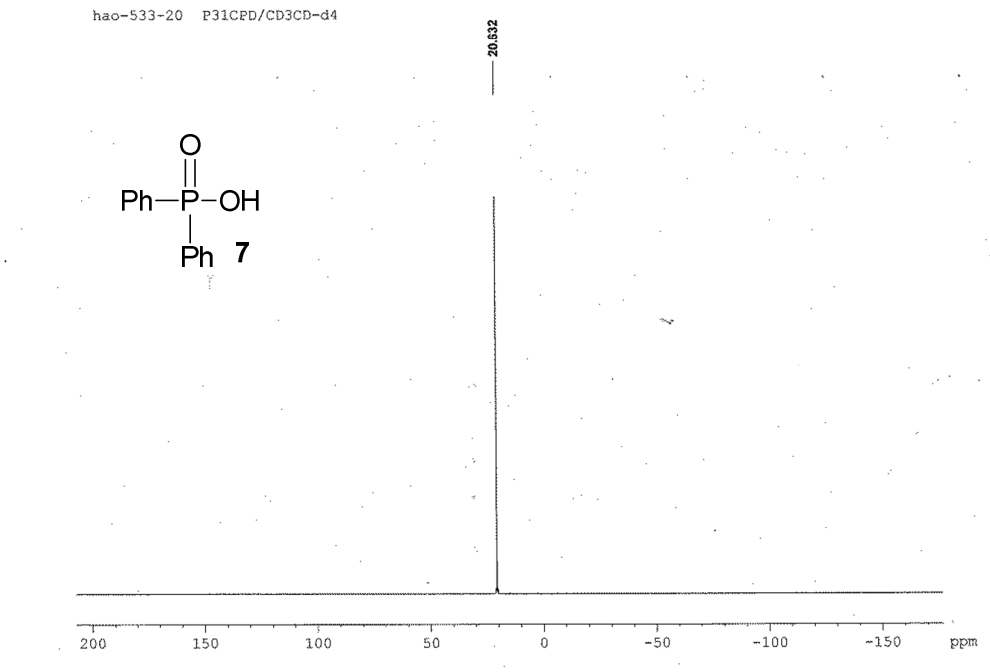
^{1}H NMR ($CDCl_3$) of **6**



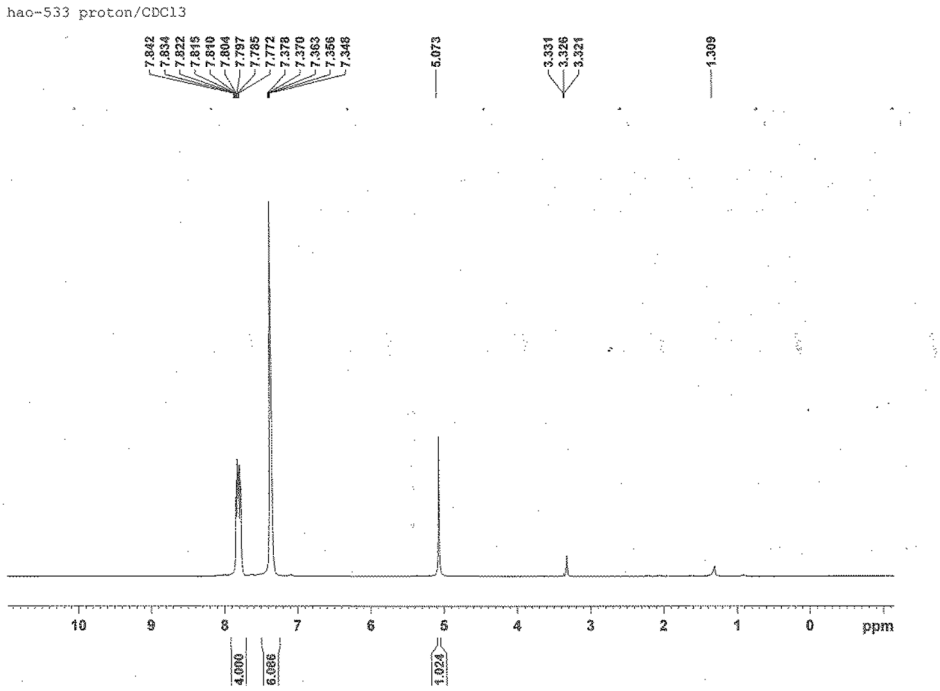
^{13}C NMR ($CDCl_3$) of **6**



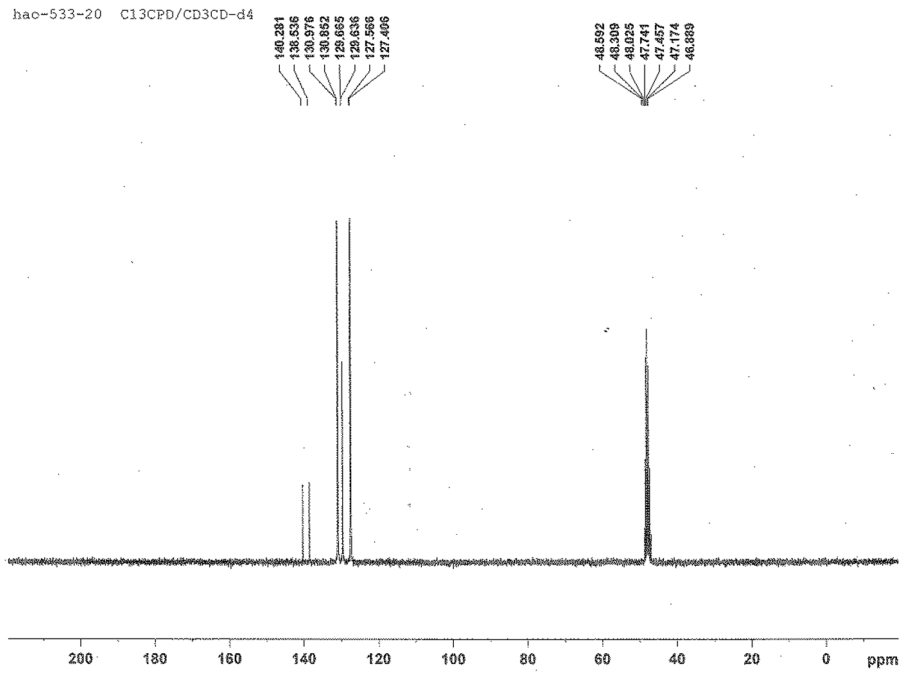
^{135}Dept NMR ($CDCl_3$) of **6**



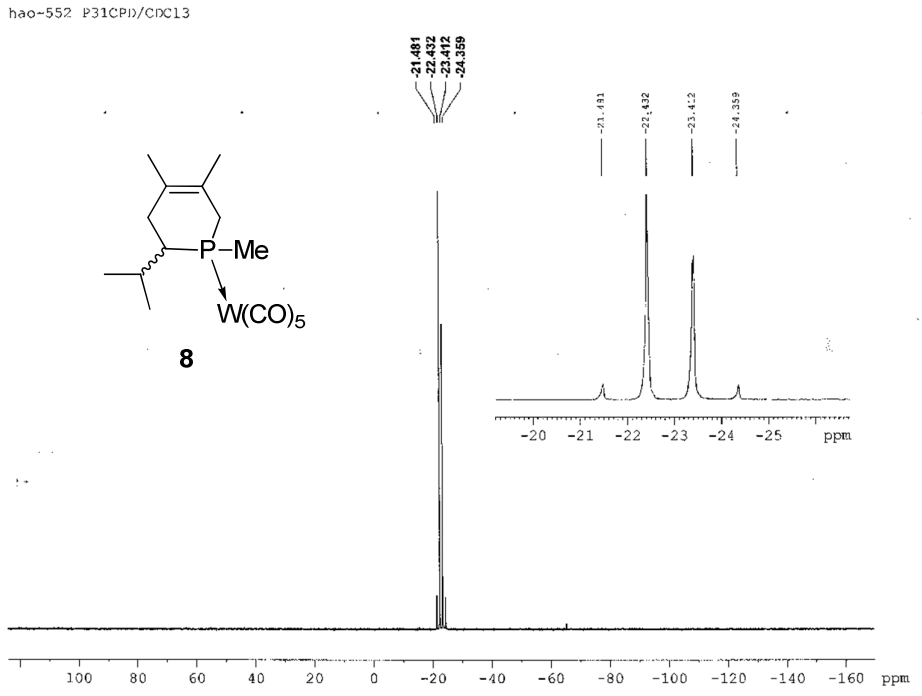
^{31}P CPD NMR ($CDCl_3$) of **7**



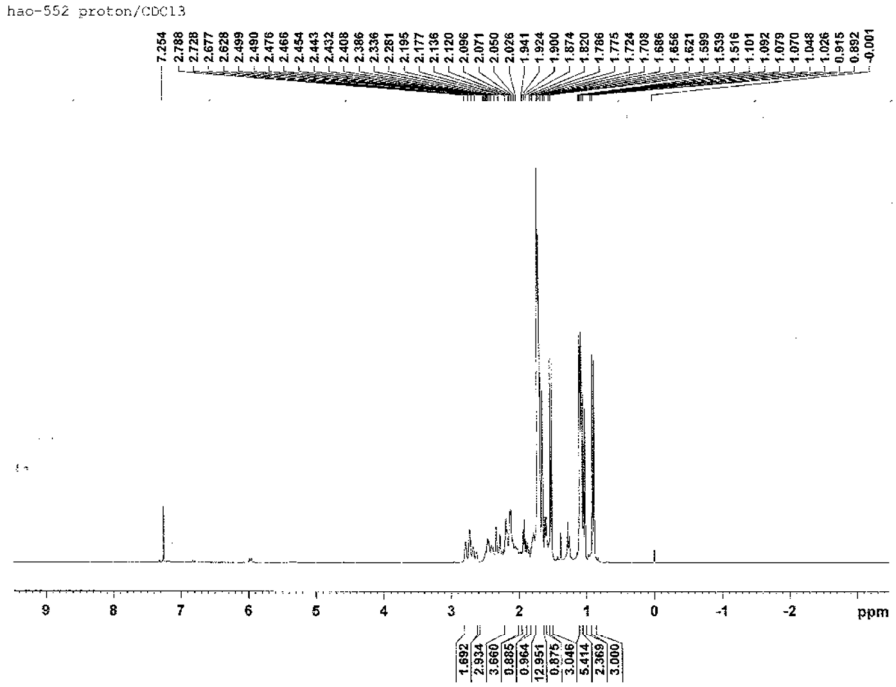
^{1}H NMR ($CDCl_3$) of **7**



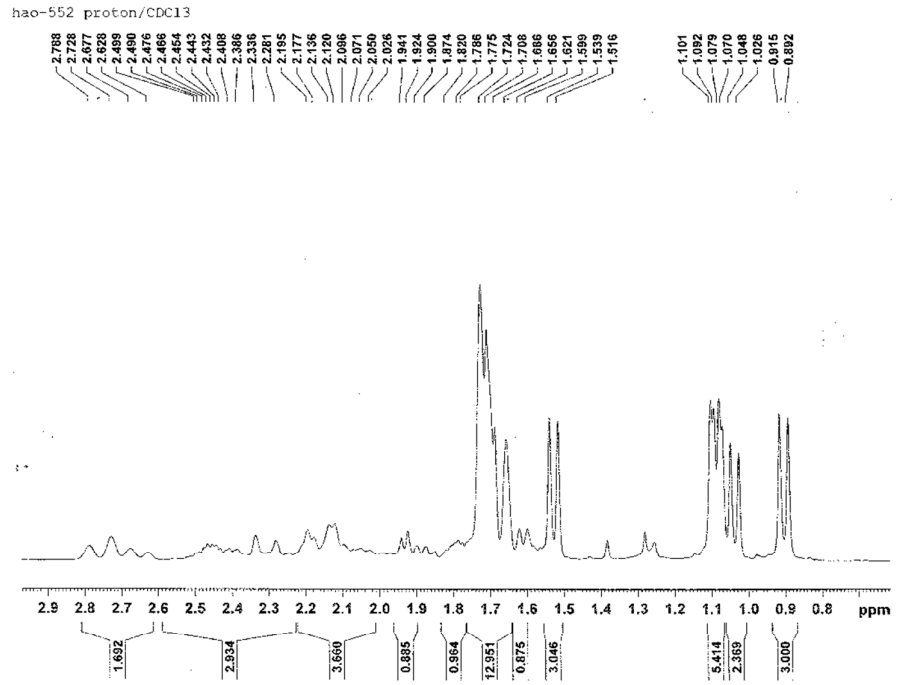
^{13}C NMR ($CDCl_3$) of **7**



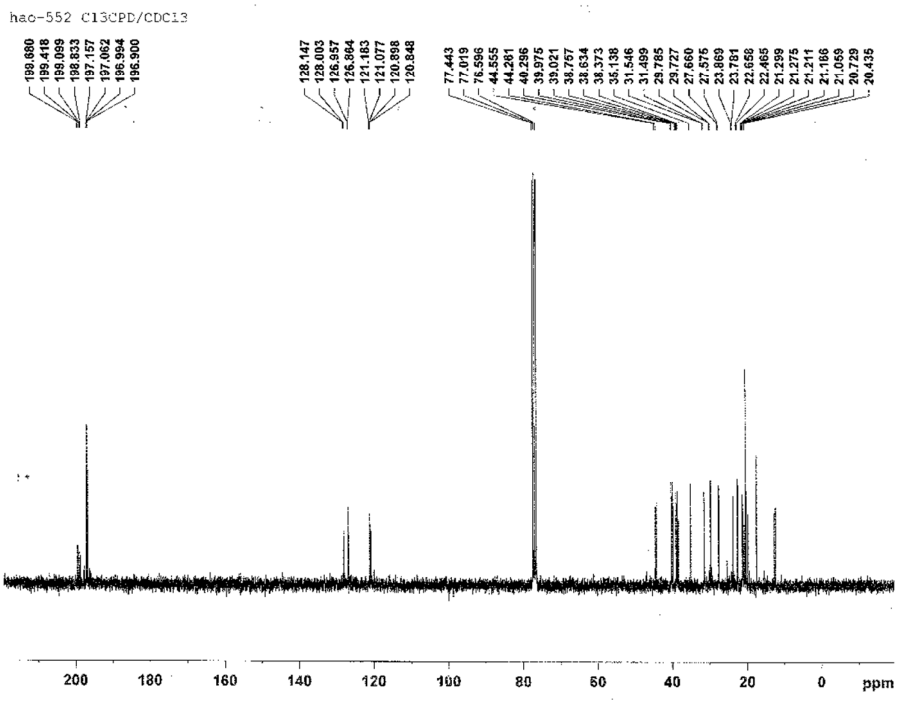
^{31}P CPD NMR ($CDCl_3$) of **8a,b**



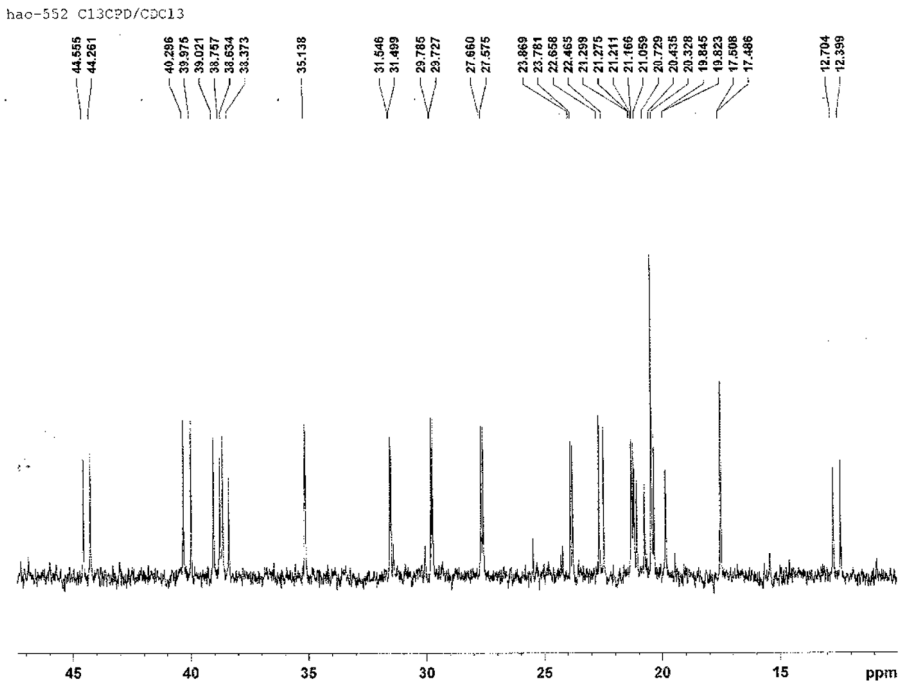
^{1}H NMR ($CDCl_3$) of **8a,b**



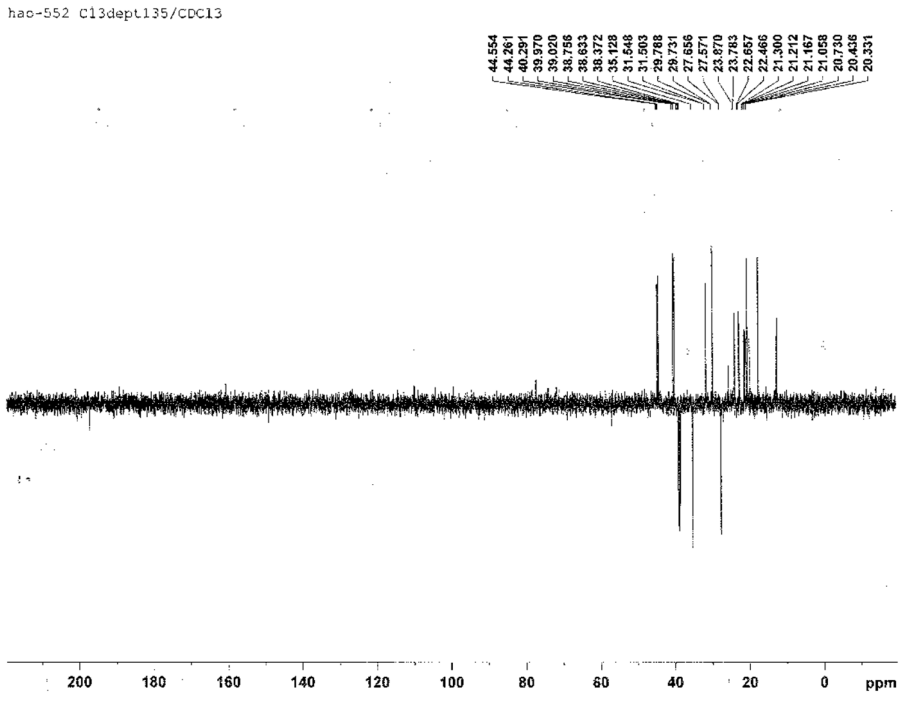
^{1}H NMR ($CDCl_3$) of **8a,b**



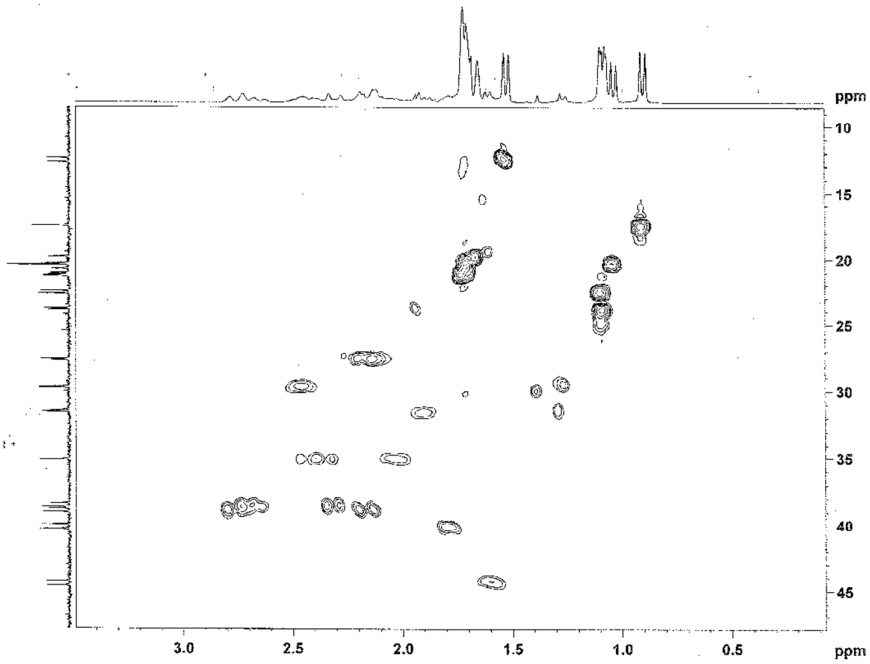
^{13}C NMR ($CDCl_3$) of **8a,b**



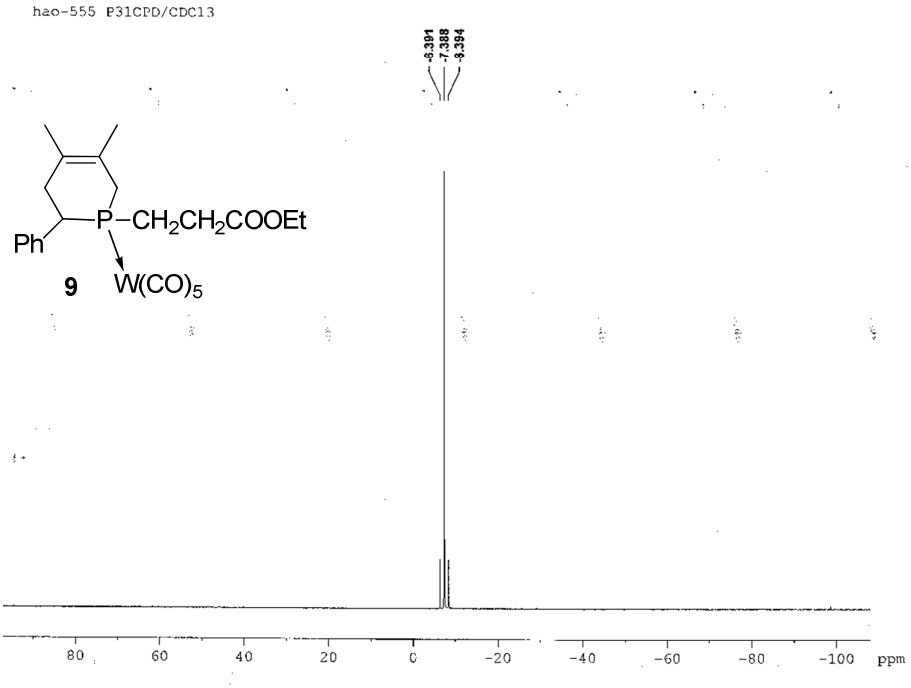
^{13}C NMR ($CDCl_3$) of **8a,b**



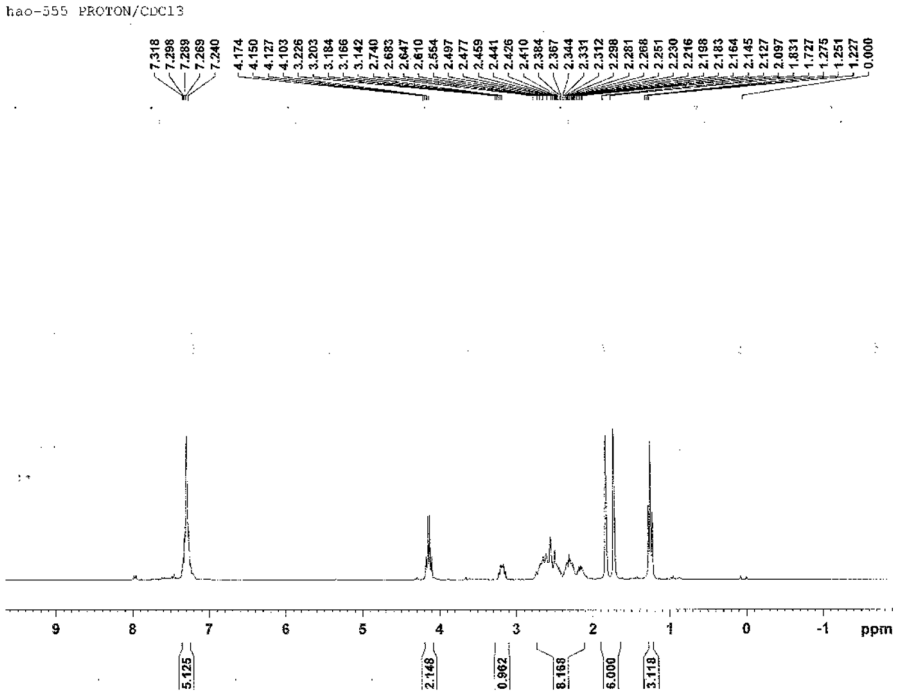
^{135}Dept NMR ($CDCl_3$) of **8a,b**



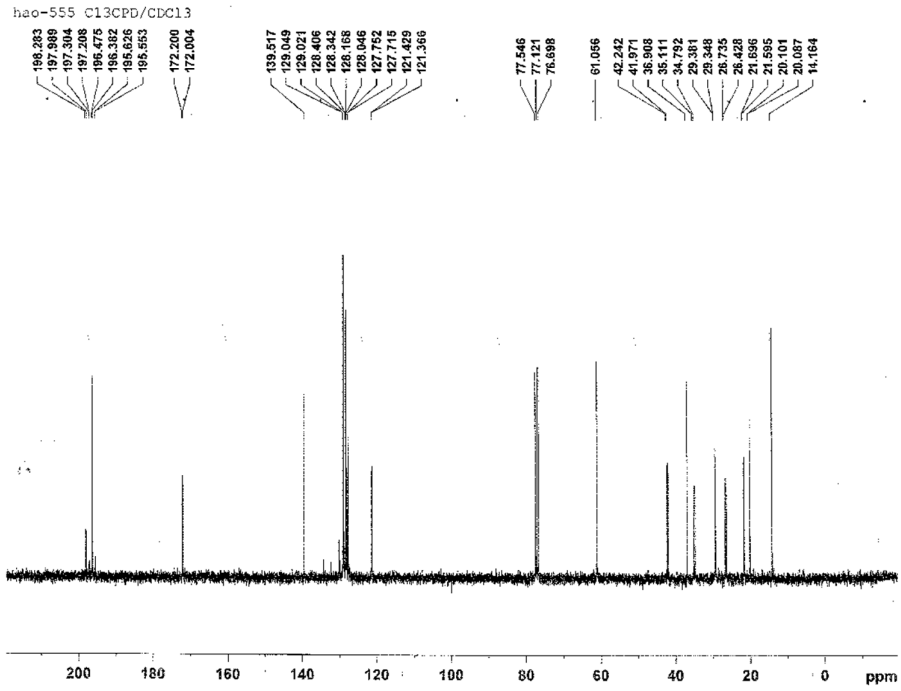
HSQC(C-H) NMR ($CDCl_3$) of **8a,b**



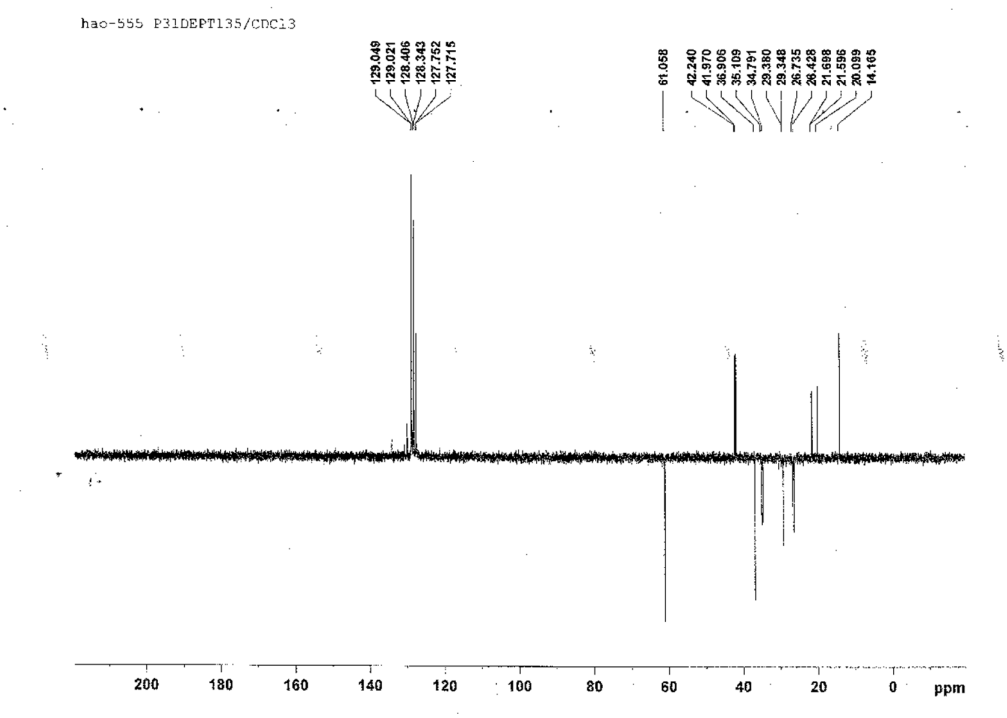
^{31}P CPD NMR ($CDCl_3$) of **9**



^{1}H NMR ($CDCl_3$) of **9**



^{13}C NMR ($CDCl_3$) of **9**



^{135}Dept NMR ($CDCl_3$) of **9**